

Herrn Prof. Dr. Adolf von Baeyer  
für persönliche Erinnerung  
an.

W. H. Perkin jun.

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[Researches in organic chemistry

by  
William Henry Perkin.

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THE CONDENSATION OF ETHYLIC TRIMETHY-  
LENEDICARBOXYLATE WITH ETHYLIC  
MALONATE.

BY

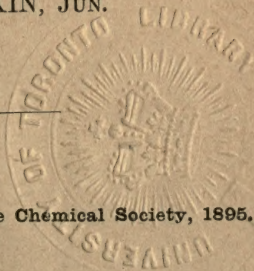
W. A. BONE, PH.D.,

AND

W. H. PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1895.]



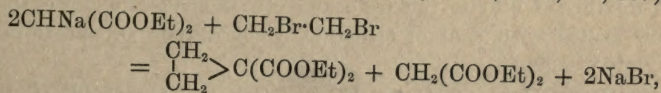
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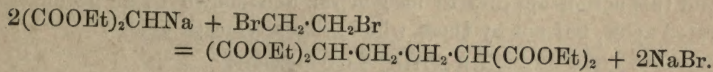
The condensation of ethylic trimethylenedicarboxylate with ethylic malonate.

By W. A. BONE, Ph.D., and W. H. PERKIN, jun.

WHEN the sodium derivative of ethylic malonate is digested in alcoholic solution with ethylene bromide, the principal product of the action is ethylic trimethylenedicarboxylate (Trans., 1885, **47**, 807),



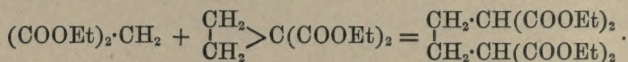
but at the same time, ethylic butanetetracarboxylate is formed in small quantity,



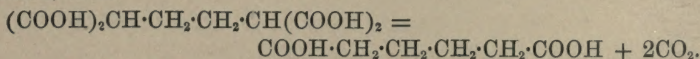
Although the amount of this ethereal salt, thus obtained, is always very small, seldom being more than 3 per cent. of the theoretical, it is so valuable for synthetical work that numerous experiments were made, with the object of improving the yield, and ultimately a satisfactory method was devised, which is described in detail in a paper published a short time since (Trans., 1894, **65**, 578). It was there shown that, if ethylene chloride be used instead of ethylene bromide, a distinct increase in the yield of ethylic butanetetracarboxylate is obtained; but the principal product in this case also appears to be ethylic trimethylenedicarboxylate, much ethylic malonate being recovered unchanged. If, now, the mixture of the



two substances, thus recovered, be again heated with sodium ethoxide and ethylene chloride, as described in detail in the paper referred to, the yield of ethylic butanetetracarboxylate is enormously increased, amounting, as it frequently does, to 50 per cent. of the product.\* The reason for this remarkable increase has now been ascertained, and it has been found that the addition of ethylene chloride in the second instance is unnecessary; for when ethylic trimethylenedicarboxylate and ethylic malonate are heated with sodium ethoxide, they react readily, forming ethylic butanetetracarboxylate.

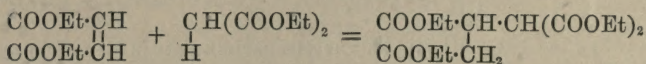


That the product really has this constitution is readily proved by hydrolysing it with alcoholic potash and subsequently heating the butanetetracarboxylic acid at 200°, when adipic acid is quantitatively formed, thus.

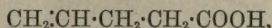


It is a well-known fact that the ethereal salts of unsaturated acids, in which the double or treble linking is situated between two carbon atoms, one of which is directly united to the carboxyl group, readily act on ethylic malonate in the presence of sodium ethoxide, with formation of condensation products (Michael, *J. pr. Chem.*, **35**, [2], 349; Auwers, *Ber.*, 1891, **24**, 307, 1923, 2887; and others).

A mixture of ethylic fumarate and ethylic malonate, for example, when heated with sodium ethoxide, yield ethylic propanetetracarboxylate,†



and this action appears to be general, and shown by all  $\alpha\beta$ -unsaturated acids, but not by those which, like allylacetic acid,



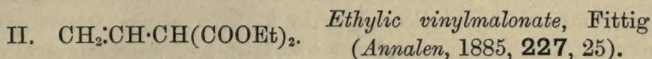
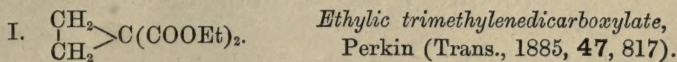
contain the double linking in any other position.

Obviously, then, in condensing with ethylic malonate to form ethylic butanetetracarboxylate, ethylic trimethylenedicarboxylate behaves exactly as if it were the ethereal salt of an  $\alpha\beta$ -unsaturated acid, and this remarkable condensation is very interesting in view of its bearing on the constitution of ethylic trimethylenedicarboxylate.

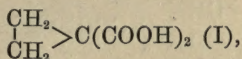
\* In the description of this process (*loc. cit.*, p. 579, line 9), instead of "four bottles," read "eight bottles."

† In all these actions, for the sake of simplicity, the intermediate formation of the sodium derivatives of the ethereal salts has not been represented.

As representing the constitution of this product of the action of ethylene bromide on ethylic malonate, two formulæ have been proposed, namely.



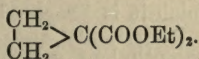
The dibasic acid derived from this ethereal salt, on hydrolysis, must, therefore, be either trimethylenedicarboxylic acid,



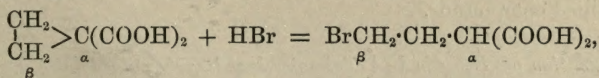
or vinylmalonic acid,  $\text{CH}_2:\text{CH}:\text{CH}(\text{COOH})_2$  (II).

As the result of a long series of investigations, it has been clearly proved that these substances are trimethylene derivatives, and not unsaturated compounds, and this view is now generally adopted (see *Beilstein's Handbuch*, Band I, 711, and Victor Meyer und Paul Jacobson, *Lehrbuch der Organischen Chemie*, Band II, 18).

No doubt, in many respects, these and other trimethylene derivatives behave like unsaturated compounds,\* forming additive compounds with bromine, hydrogen bromide, sulphuric acid, &c., whilst, on the other hand, they exhibit properties which preclude the possibility of their being ordinary unsaturated compounds, and, in fact, their whole behaviour is in complete harmony with their constitution as trimethylene derivatives, as Baeyer has indicated in his "Spannung's Theorie" (*Ber.*, 1885, 18, 2277; compare Trans., 1894, 951). The formation of ethylic butanetetracarboxylate from ethylic malonate and ethylic trimethylenedicarboxylate, as described above, is a further proof of the correctness of this view, and can only be explained on the assumption that the latter ethereal salt has the constitution



When trimethylenedicarboxylic acid yields additive products, it behaves exactly as if it were an  $\alpha\beta$ -unsaturated acid; for example, with hydrogen bromide it yields  $\omega$ -bromomethylmalonic acid,



\* It is the intention of one of us, on a future occasion, to give a short summary of the methods of formation and of the properties of trimethylene compounds, in order, if possible, to show clearly the points of similarity and difference between these compounds and unsaturated substances.







sure for 8—10 hours at  $100^{\circ}$ ; the details of the process are similar to those already given (Trans., 1885, 47, 808), about 350 grams of ethylic malonate being used. The product, after being extracted with ether in the usual way, was very carefully fractionated at ordinary pressure, and about 240 grams, distilling over between  $180^{\circ}$  and  $225^{\circ}$ , collected. This fraction was mixed with a solution of 17 grams of sodium in absolute alcohol and 72 grams of ethylene dibromide, and the mixture heated in three soda-water bottles at  $100^{\circ}$  for five hours; the product, isolated and extracted in the usual manner, was submitted to a careful fractionation under the ordinary pressure. About 195 grams distilled between  $180^{\circ}$  and  $225^{\circ}$ , of which at least two-thirds came over above  $200^{\circ}$ . Of this fraction, approximately one-third was considered to consist of unchanged ethylic malonate and two-thirds of ethylic trimethylenedicarboxylate (b. p.  $208^{\circ}$ ).

Fifty grams of this product were now mixed with 30 grams of ethylic malonate, the mixture added to a solution of 7 grams of sodium dissolved in 90 grams of absolute alcohol, and this solution of ethylic trimethylenedicarboxylate with the sodium derivative of ethylic malonate heated in soda-water bottles at  $100^{\circ}$  for eight hours. As much as possible of the alcohol having been distilled off, the dark red residue was mixed with water and acidified with dilute hydrochloric acid; the thick, reddish oil which separated was extracted with ether, and the ethereal solution, after being well washed with water and dilute sodium carbonate solution, was dried over calcium chloride, and the ether distilled off. The residual red oil was now fractionated under reduced pressure (40 mm.), when about a quarter of the whole passed over below  $180^{\circ}$ , and was found, on examination, to consist of a mixture of ethylic 1:1-trimethylenedicarboxylate and ethylic malonate. The temperature then rose rapidly, and from 60 to 70 grams passed over between  $210^{\circ}$  and  $240^{\circ}$ . A small quantity of this oil, collected at  $238$ — $240^{\circ}$  (40 mm.), gave the following results on analysis, showing it to consist of ethylic butanetetracarboxylate.

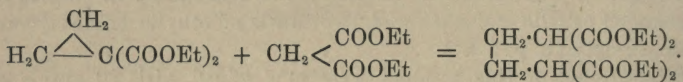
	Found.	Theory. $C_{16}H_{26}O_8$ .
C .....	55.21 per cent.	55.49 per cent.
H .....	7.60       ,,	7.51       ,,

*Hydrolysis of the Oil.*—In order to prove that this oil was ethylic butanetetracarboxylate, it was mixed with three times its volume of concentrated hydrochloric acid, glacial acetic acid added until the oil just dissolved, and the whole digested several hours in a reflux apparatus on a sand bath; steam was then driven through the liquid until the whole of the acetic acid had been removed, and the solution filtered and evaporated to a small bulk on the water bath. After

a time, crystals formed; these were separated from the mother liquor, redissolved in water, and the aqueous solution boiled with animal charcoal; the solution was then filtered and concentrated until crystallisation commenced. On standing, colourless crystals were deposited, which melted at  $149^\circ$ , and resembled adipic acid in all respects. Analysis.

	Found.	Theory. $C_6H_{10}O_4$ .
C .....	49.01 per cent.	49.31 per cent.
H .....	6.87     ,,	6.85     ,,

This formation of adipic acid proves conclusively that ethylic butanetetracarboxylate had been formed by the condensation of ethylic trimethylenedicarboxylate with ethylic malonate, thus.



We have also prepared ethylic butanetetracarboxylate from the low boiling product of the action of ethylene dichloride on the sodium derivative of ethylic malonate (Trans., 1894, **65**, 579). For this purpose, 94 grams of the product which, after a second fractionation, distilled over between  $200^\circ$  and  $230^\circ$  (under ordinary atmospheric pressure), was mixed with a solution of 6.5 grams of sodium in 80 grams of absolute alcohol, and heated for nine hours at  $100^\circ$  in a soda-water bottle. It was then poured into water, the solution acidified with dilute hydrochloric acid, and the heavy oil which separated extracted with ether; the ethereal solution, after being washed with a dilute solution of sodium carbonate and with water, was dried over calcium chloride, and the ether distilled off. The oily residue was first distilled under the ordinary pressure, when 30 grams came over below  $230^\circ$ ; the distillation was then continued under reduced pressure (70 mm.), when the oil began to pass over at  $180^\circ$ , and two fractions were collected, one at  $180$ — $225^\circ$ , and the other at  $225$ — $240^\circ$ .

This higher fraction ( $225$ — $240^\circ$ ), when hydrolysed by means of a mixture of concentrated hydrochloric and glacial acetic acids in the manner already described, yielded colourless crystals melting at  $149.5^\circ$ , and possessing all the properties of adipic acid.

Analysis of the acid gave the following numbers.

	Found.	Calculated for adipic acid.
Carbon .....	48.84 per cent.	49.31 per cent.
Hydrogen .....	6.73     ,,	6.85     ,,



*Condensation of Ethylic Trimethylenedicarboxylate with Ethylic Methylmalonate. Formation of Ethylic Methylbutanetetracarboxylate,*  
 $(\text{COOEt})_2\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})_2$ .

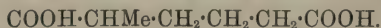
In order to bring further evidence in support of this remarkable property of ethylic trimethylenedicarboxylate, experiments were tried with the object of obtaining a condensation product from this compound and ethylic methylmalonate. In doing this, it was found to be unnecessary to isolate the ethylic trimethylenedicarboxylate, provided all the ethylic malonate in the mixture of this substance with ethylic trimethylenedicarboxylate (p. 112) was converted into the mono- or di-methyl derivative. To effect this, 180 grams of the mixture was added to a solution of 12·6 grams of sodium in 160 grams of ethylic alcohol, then 80 grams of methylic iodide, and the whole heated on the water bath in a reflux apparatus for one hour; in this way, the ethylic malonate present was completely transformed into the mono- or di-methyl derivative, the large quantity of sodium ethylate and methylic iodide employed ensuring the complete conversion of the ethylic malonate. After the excess of alcohol had been distilled off on the water bath, the product was poured into water, and the oil which separated was extracted with ether. The ethereal solution, after being well washed with a dilute solution of sodium thiosulphate, to remove iodine, and then with water, was dried over calcium chloride, and the ether distilled off; the oily residue, on fractionation, yielded a colourless oil distilling between  $180^\circ$  and  $220^\circ$ . 90 grams of this oil was mixed with 40 grams of ethylic methylmalonate, the whole added to 12 grams of sodium dissolved in 150 grams of absolute alcohol, and the mixture heated in soda-water bottles for 10 hours at  $100^\circ$ . After distilling off as much alcohol as possible on the water bath, the product was poured into water, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal solution, after being well washed with dilute sodium carbonate solution and with water, was dried over calcium chloride, and the ether distilled off. The residual oil, when distilled under reduced pressure (40 mm.), gave 60 grams of distillate below  $180^\circ$ ; the thermometer then rose rapidly, and 25 grams came over between  $200^\circ$  and  $250^\circ$ ; the greater portion of this, when refractionated, passed over at  $240^\circ$  (40 mm.), and was analysed with the following results.

	Found.	Calculated for $\text{C}_{17}\text{H}_{28}\text{O}_8$ .
Carbon .....	56·09 per cent.	56·66 per cent.
Hydrogen .....	7·81 „	7·77 „

The oil is therefore ethylic methylbutanetetracarboxylate, and



its constitution is proved by the fact that, on hydrolysis and subsequent distillation, it yields  $\alpha$ -methyladipic acid,



*$\alpha$ -Methyladipic acid.*

*Hydrolysis of the Oil.*—Twenty-five grams of the oily ethylic methylbutanetetra-carboxylate just described were carefully added to a well-cooled solution of 25 grams of potassium hydroxide in methylic alcohol. Very little action took place in the cold, but on heating in a reflux apparatus on the water bath, the potassium salt of the acid separated in minute crystals. After heating for eight hours, the product was poured into water, the liquid evaporated until free from methylic alcohol, and the solution, which should be as concentrated as possible, was acidified with hydrochloric acid, and extracted several times with pure ether. The ethereal solution, after being dried over calcium chloride and evaporated, left a thick, almost colourless syrup, presumably methylbutanetetra-carboxylic acid. This, when distilled under reduced pressure (60 mm.), evolved carbon dioxide, a colourless acid distilling over between  $250^\circ$  and  $260^\circ$ ; the latter, on being allowed to remain over night, solidified to a white crystalline mass of nearly pure  $\alpha$ -methyladipic acid, which was spread out on a porous plate and allowed to stand for some days, until free from oily mother liquor. Great difficulty was experienced in recrystallising this acid, owing to its excessive solubility, and the slight tendency it has to crystallise, in which respect it differs in a marked manner from adipic acid. The most satisfactory results were obtained by dissolving the acid in a very small quantity of water, and evaporating in a vacuum over concentrated sulphuric acid, the thick syrup which was left deposited ill-defined nodular masses when left for a week or more in a vacuum; these were dried, first on a porous plate, then in a vacuum over sulphuric acid, and analysed.

	Found.	Theory. $\text{COOH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}.$
Carbon.....	52.10 per cent.	52.50 per cent.
Hydrogen ....	7.34     ,,	7.50     ,,

$\alpha$ -Methyladipic acid melts at about  $64^\circ$ , but this melting point must be taken as only approximate, owing to the difficulty experienced in recrystallising the acid.

It is excessively soluble in water, readily in alcohol and ether, and sparingly in cold, but readily in hot benzene or light petroleum. If the benzene solution be allowed to evaporate slowly in the air, the acid separates in stellate groups of minute foliated crystals.

*Salts of  $\alpha$ -Methyladipic acid.*

*Calcium Salt.*—This differs from the corresponding salt of adipic acid in being somewhat readily soluble in water; no precipitate is formed on adding excess of a concentrated solution of calcium chloride to a neutral solution of the ammonium salt of the acid, but on carefully concentrating the mixture on the water bath, the calcium salt separates in colourless needles.

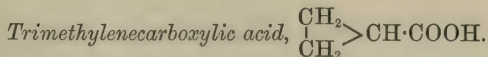
*Silver Salt.*—On adding a solution of silver nitrate to the neutral solution of the ammonium salt, a white precipitate of the silver salt is formed immediately. It is moderately soluble in hot, but only slightly in cold water. For analyses, the salt was dried, first on a porous plate, and then in a vacuum over sulphuric acid; it may be exposed to diffused daylight for several hours without any change in colour, and may be dried at  $100^{\circ}$  without any perceptible decomposition.

The salt was analysed in two ways: (I) it was decomposed by dilute nitric acid, and the silver precipitated by dilute hydrochloric acid; (II) it was carefully ignited, and the residual silver weighed.

Calculated for  $C_7H_{10}O_4Ag_2$ . Silver = 57.75 per cent.

Found ..... „ (I) 57.78; (II) 57.81 per cent.

It seemed interesting and important to ascertain whether this remarkable property of trimethylene compounds of forming additive compounds with ethylic malonate is shared by the corresponding tetramethylene derivatives. We accordingly prepared ethylic 1:1-tetramethylenedicarboxylate by the action of trimethylene bromide on the sodium compound of ethylic malonate, the details of the method have already been given by one of us (*Trans.*, 1887, **51**, 2). This was then mixed with the calculated quantity of ethylic malonate and sodium ethylate, in alcoholic solution, and the whole was heated in a sealed tube for nine hours at  $100^{\circ}$ . On isolating the product in the usual manner, it was found to consist entirely of ethylic malonate and tetramethylenedicarboxylate. Evidently, then, under these circumstances detailed in this paper, the tetramethylene is much more stable than the trimethylene ring.



The properties of this important derivative of trimethylene have, so far, not been carefully studied,\* and it therefore appeared to us that it would be interesting to prepare as pure a sample as possible

\* The work already done on this acid is contained in the following papers: Fittig and Roeder, *Annalen*, 1885, **227**, 25; W. H. Perkin, jun., *Ber.*, 1884, **17**, 57; and 1885, **18**, 1738; *Trans.*, 1885, **47**, 815.

of the substance, in order that its physical constants might be determined.

For this purpose, 1 : 1-trimethylenedicarboxylic acid was highly purified and submitted to distillation; the distillate, consisting of a mixture of trimethylenedicarboxylic acid and butyrolactone, was then dissolved in water, sodium carbonate added until the liquid was alkaline, and the butyrolactone removed by repeated extraction with purified ether. The alkaline solution was next acidified, and the trimethylenedicarboxylic acid extracted with pure ether; the ether having been distilled off, the treatment with sodium carbonate was repeated, in order to remove the last traces of butyrolactone, and the acid finally purified by careful fractionation.

The portion boiling at 182–183°—that used in the experiment described below—gave the following results on analysis.

	Found.	Theory. $C_4H_6O_2$ .
C .....	55.57 per cent.	55.81 per cent.
H .....	7.13 „	6.98 „

Trimethylenedicarboxylic acid is miscible with water in all proportions; the “dissociation constant” was kindly determined by Dr. Walker, who found  $\kappa = 0.0014$ ; but the results were not quite so sharp as could have been wished, owing, possibly, to slight decomposition of the acid in aqueous solution.

The determinations of the density, magnetic rotation, and refractive power of this acid were carried out by W. H. Perkin, sen., with the following results.

#### *Relative Density Determinations.*

$d\ 4^\circ/4^\circ = 1.1024.$	$d\ 10^\circ/10^\circ = 1.0966.$	$d\ 15^\circ/15^\circ = 1.0923.$
$d\ 20^\circ/20^\circ = 1.0884.$	$d\ 25^\circ/25^\circ = 1.0848.$	

#### *Magnetic Rotation.*

This was twice determined, and the numbers given are the mean of 64 readings.

$t$ .	Sp. rotation.	Mol. rotation.
18.6°	0.9443	4.141

The value estimated as butyric acid minus  $H_2$ , assuming the acid to be saturated, is 3.964; on the other hand, an unsaturated acid of this formula would have the calculated value 5.584.  $\alpha$ -Crotonic acid,  $CH_3 \cdot CH : CH \cdot COOH$ , calculated from the magnetic rotation of its ethylic salt, has the value 5.589. These numbers, therefore, prove clearly that trimethylenedicarboxylic acid cannot be an unsaturated acid.



*Refractive Power.*

Line.	$\mu$ .	$\frac{\mu - 1}{d}$ .	$\frac{\mu - 1}{d} p$ .
A.....	1.43196	0.39649	34.098
H <sub>a</sub> .....	1.43500	0.39928	34.338
D .....	1.43763	0.40170	34.546
H <sub><math>\beta</math></sub> .....	1.44388	0.40743	35.039
H <sub><math>\gamma</math></sub> .....	1.44910	0.41222	35.451
H (estimated) ..	—	—	35.800

The *dispersion* H — A is about 1.70.

The formula  $C_4H_6O_2$ , estimated for A by Gladstone's value, requires, if saturated, 34.00, if unsaturated, 35.10; by Brühl's value for H<sub>a</sub>, if saturated, 34.00, but if unsaturated, 36.3. The experimental result thus confirms the constitution deduced from the magnetic rotation determinations, showing that trimethylenecarboxylic acid cannot be an unsaturated compound.

In connection with this point, the behaviour of this acid towards permanganate in alkaline solution is also interesting.

If the pure acid be dissolved in a slight excess of sodium carbonate at 0°, the solution will not decolorise permanganate at once, but does so on long standing, and very rapidly if the solution is gently warmed. The acid is much more stable towards permanganate than an unsaturated acid, but is, on the other hand, much more readily oxidised than the corresponding tetramethylenecarboxylic acid; this is what might be expected, from the study of the chemical properties of the two acids.

*Action of Hydrogen Bromide on Trimethylenecarboxylic acid. Formation of  $\gamma$ -Bromobutyric acid,  $CH_2Br \cdot CH_2 \cdot CH_2 \cdot COOH$ .*

Trimethylenecarboxylic acid dissolves readily in fuming hydrobromic acid with slight development of heat, and there is apparently little action in the cold; on heating in a sealed tube at 175°, however, decomposition takes place readily, and the contents of the tube separate into two layers. The product was poured into water, the oily layer extracted with ether, and the ethereal solution well washed with water and dried over calcium chloride; on evaporating, an almost colourless oil was obtained, which solidified to a mass of crystals on cooling; these, after standing over sulphuric acid in a vacuum, in contact with porous porcelain, became colourless, and, on analysis, gave the following results.

	Found.	Theory. $C_4H_7BrO_2$ .
Br .....	48.32 per cent.	47.90 per cent.

This substance melts at 33—35°, and is obviously identical with

the  $\gamma$ -bromobutyric acid, melting at 32—33°, obtained by Henry (*Bull. Soc. Chim.*, **46**, 65) from  $\gamma$ -butyrolactone, by the action of hydrobromic acid.

This experiment shows that trimethylenedicarboxylic acid and trimethylenemonocarboxylic acid behave similarly when treated with hydrobromic acid, both yielding  $\gamma$ -bromo-additive products.

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Manchester.*

# DERIVATIVES OF TETRAMETHYLENE.

BY

W. H. PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1894.]





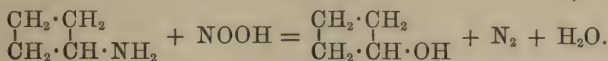
## Derivatives of tetramethylene.

By W. H. PERKIN, jun.

THE close relationship which exists between tetramethylenecarboxylic acid  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$  and the fatty acids, especially the valeric acids, not only in physical properties, but also in general chemical behaviour, has been frequently pointed out; and, in view of this close agreement, the statement of Freund and Gudeman (*Ber.*, **21**, 2695), that the amide of tetramethylenecarboxylic acid on treatment with bromine and potash does not yield more than traces of tetramethyleneamine,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{array}$ , seemed remarkable, especially when it is remembered that under similar conditions 90 per cent. of the theoretical yield of isobutylamine is obtained from the amide of isovaleric acid (Hofmann, *Ber.*, **15**, 769).

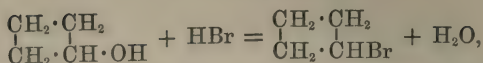
In order to investigate the cause of this difference in behaviour, numerous experiments on this reaction were made, and it was found that when the *pure* amide of tetramethylenecarboxylic acid (melting at 152—153°) is employed, an excellent yield of tetramethyleneamine is obtained; on the other hand, an impure amide, such as was used by Freund and Gudeman (they give the melting point of 138°), gives only traces of the base under the same conditions.

Tetramethyleneamine,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{NH}_2 \end{array}$ , is a colourless liquid which boils at 81°, and closely resembles isoamylamine in general properties; it has a strong, basic odour, mixes with water with development of heat, and gives beautifully crystalline salts, of which the *hydrochloride*,  $\text{C}_4\text{H}_9\text{N} \cdot \text{HCl}$ , and the *platinochloride*,  $(\text{C}_4\text{H}_9\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , were analysed: the former salt, when treated with silver nitrite in aqueous solution, is converted almost quantitatively into hydroxy-tetramethylene.



This secondary alcohol boils at 123° and shows the closest resemblance to the fatty alcohols containing the same number of carbon atoms; it might, indeed, be readily mistaken for normal butylic alcohol.

When digested with fuming hydrobromic acid, hydroxytetramethylene behaves in a remarkable manner, as although it is in part converted into *bromotetramethylene*, a colourless oil boiling at 104°, and closely resembling butylic bromide in properties,



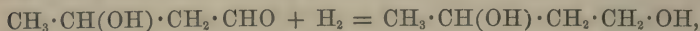
the principal product is a dibromobutane,  $\text{C}_4\text{H}_8\text{Br}_2$ , boiling at  $173-174^\circ$ , which must have been formed by the disruption of the four-carbon ring,



a behaviour which, so far, has only been observed in the case of trimethylene and some of its derivatives.

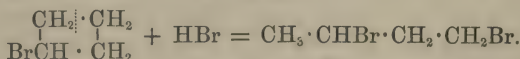
As none of the dibromobutanes,\* which had, so far, been prepared, agreed in their properties with the product obtained from hydroxytetramethylene, experiments were instituted with the object of synthesising the missing members of the series, and in this way determining with which of them this dibromobutane was identical. Ultimately, the required isomeride was obtained as follows.

Aldol was reduced, in neutral solution, with sodium amalgam and thus converted into 1 : 3-dihydroxybutane,



and this, when treated with hydrobromic acid, yielded 1 : 3-dibromobutane,  $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$ , which boils at  $174^\circ$ , and was found to be identical in all respects with the dibromide obtained from hydroxytetramethylene.

In the formation of this dibromobutane from hydroxytetramethylene, it is probable that bromotetramethylene is first produced, which then reacts with a further quantity of hydrobromic acid with disruption of the tetramethylene ring, thus :



That the tetramethylene ring may be split in this way is a very interesting fact when taken in connection with Baeyer's view of the stability of rings as developed by him in his well-known "Spannung's Theorie" (*Ber.*, 18, 2277), which is, briefly stated, as follows.

If it be supposed that the four affinities of the carbon-atom act in the direction of lines drawn from the centre of a tetrahedron to the

\* This will be readily seen from the following table, which gives the known isomerides with their boiling points :—

1 : 2	Dibromobutane, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$	B. p. $166^\circ$
1 : 4	„ $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$	„ $190$
2 : 2	„ $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CBr}_2 \cdot \text{CH}_3$	„ $145$
2 : 3	„ $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CH}_3$	„ $158$
1 : 3	Dibromobutane, $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$	obtained as explained above boils at $174^\circ$ .



corners, then these directions are inclined to one another at an angle of  $109^{\circ} 28'$ .

When such carbon-atoms combine together to form a closed chain the direction of these affinities must be altered, and to do this a certain strain ("Spannung") must be applied, which may be measured by the angle through which the line of affinity is supposed to be deviated.

In the case of trimethylene  $\text{H}_2\text{C} \triangle \text{CH}_2$ , for example, in which the carbon-atoms are assumed to be situated at the corners of an equilateral triangle, the angles between two affinities of each carbon-atom forming the ring is  $60^{\circ}$ , that is to say, the direction of each affinity has been displaced through an angle of  $\frac{1}{2}(109^{\circ} 28' - 60^{\circ}) = 24^{\circ} 44'$ ; in

the formation of the tetramethylene ring,  $\begin{array}{cc} \text{H}_2\text{C} & \text{CH}_2 \\ | & | \\ \text{H}_2\text{C} & \text{CH}_2 \end{array}$ , the angle of displacement is much less, *e.g.*,  $\frac{1}{2}(109^{\circ} 28' - 90^{\circ}) = 9^{\circ} 44'$ .

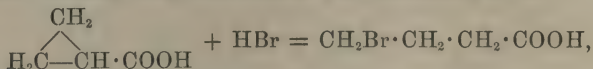
The following table, taken from Baeyer's paper, shows the deviation of the direction of each affinity of the carbon-atom necessary in combining with other carbon-atoms to form rings.

$\begin{array}{c} \text{CH}_2 \\    \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \triangle \\ \text{H}_2\text{C} - \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\   \quad   \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \\   \quad   \\ \text{H}_2\text{C} - \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \\   \quad   \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$
+ $54^{\circ} 44'$	+ $24^{\circ} 44'$	+ $9^{\circ} 44'$	+ $0^{\circ} 44'$	- $5^{\circ} 16'$

In ethylene, the deviation is greatest, and the tendency of the ring to open out with formation of additive products would, therefore, be assumed to be very pronounced; and this is found experimentally to be the case, since ethylene combines with the greatest ease with hydrogen bromide, bromine, chlorine, and even iodine; in the case of trimethylene, the deviation is very much less, and this gas, although it combines with hydrogen bromide and with bromine with disruption of the ring, does so with much greater difficulty than ethylene; chlorine does not act on trimethylene at all except in the presence of sunlight, and then the principal products of the action are the substitution products, monochlorotrimethylene,  $\text{C}_3\text{H}_5\text{Cl}$ , and dichlorotrimethylene,  $\text{C}_3\text{H}_4\text{Cl}_2$ , some trimethylene chloride,  $\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ , and other products being, however, also produced (Gustavson, *J. pr. Chem.*, 1894, 50, 380).

In accordance with Baeyer's theory, the tetramethylene ring should be much more stable than the trimethylene ring, and this is clearly proved to be the case from a comparison of the properties of some of the derivatives of these hydrocarbons.

Trimethylenecarboxylic acid, for example, is readily acted on by hydrogen bromide with formation of  $\gamma$ -bromobutyric acid,



whereas tetramethylenecarboxylic acid is not decomposed even when heated with fuming hydrobromic acid at  $150^\circ$ , and many other similar cases might be cited; on the other hand, bromotetramethylene is decomposed by boiling concentrated hydrobromic acid, but comparatively slowly.

This difference in the behaviour of bromotetramethylene and tetramethylenecarboxylic acid is very remarkable, the nature of the substituting groups obviously having a very pronounced effect on the stability of the ring; this same difference of stability is also very marked in the case of the trimethylene compounds, as will be shown in a subsequent paper.

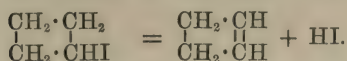
It would be exceedingly interesting to study the behaviour of pentamethylene and hexamethylene and their derivatives towards hydrobromic acid, as, according to Baeyer's theory, the former, owing to the slight strain necessary for its formation, would probably not be attacked; this, moreover, seems to be true, since pentamethylene-1:2-dicarboxylic acid, for example, may be heated with hydrobromic acid at  $150^\circ$  without change.

Hexamethylene and its derivatives might under similar conditions be decomposed, but probably not so readily as tetramethylene compounds, and the behaviour of these substances would be an important test of the value of the "Spannung's Theorie."

In connection with this point, it should be noted that benzene, when heated at  $260$ — $270^\circ$ , with hydriodic acid containing iodine, yields hexane (comp. Baeyer, *Annalen*, **278**, 89) with disruption of the ring. Possibly, in this case, hexamethylene iodide,  $\text{C}_6\text{H}_{12}\text{I}_2$ , or diiodide,  $\text{C}_6\text{H}_{12}\text{I}_2$ , may first be produced, and then reduced to hexane by the further action of the hydriodic acid.

Chlorotetramethylene,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CHCl} \end{array}$ , may be readily obtained by the action of phosphorus pentachloride on hydroxytetramethylene. It is a colourless oil which boils at  $85^\circ$ , and when treated with potassium iodide in alcoholic solution yields iodotetramethylene,  $\text{C}_4\text{H}_7\text{I}$  (b. p.  $138^\circ$ ), although the action does not take place readily. The last-named substance was prepared in considerable quantity (30 grams), in the hope that tetramethylene might be obtained from it by reduction under suitable conditions, and that by treatment with quinoline (Baeyer, *Annalen*, **278**, 107), dihydrotetrene\* might be formed, thus.

\* With regard to this nomenclature, see *Trans.*, 1890, **57**, 214.



The preliminary experiments gave results which seemed to bear out these suppositions; but, on the other hand, it was soon evident that a detailed examination of such hydrocarbons, which would probably boil at about 20° and 35° respectively, could only be carried out with such quantities of material as it would be almost impossible to obtain by the methods described in this paper, and therefore this part of the subject was not further investigated.

The close resemblance of chloro-, bromo-, and iodo-tetramethylene to the corresponding butyl compounds is very marked, as will be seen from a comparison of their properties. The tetramethylene compounds all boil somewhat higher than the butyl compounds, and this is also noticeable in the case of other tetramethylene derivatives, which all, without exception, boil higher than the corresponding saturated fatty compounds, as is seen from the following table, in which the symbol  $\square$  is used for  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \end{array}$ .

Tetramethylene derivatives.	B. p.	Butane derivatives.	B. p.	Diff.
$\square \cdot \text{COOH} \dots\dots\dots$	195°	$\text{C}_4\text{H}_9 \cdot \text{COOH} \dots\dots\dots$	186°	+9°
$\square \cdot \text{NH}_2 \dots\dots\dots$	81	$\text{C}_4\text{H}_9 \cdot \text{NH}_2 \dots\dots\dots$	76	+5
$\square \cdot \text{OH} \dots\dots\dots$	123	$\text{C}_4\text{H}_9 \cdot \text{OH} \dots\dots\dots$	116	+7
$\square \cdot \text{Cl} \dots\dots\dots$	85	$\text{C}_4\text{H}_9\text{Cl} \dots\dots\dots$	77	+8
$\square \cdot \text{Br} \dots\dots\dots$	104	$\text{C}_4\text{H}_9\text{Br} \dots\dots\dots$	100	+4
$\square \cdot \text{I} \dots\dots\dots$	138	$\text{C}_4\text{H}_9\text{I} \dots\dots\dots$	131	+7

Other examples illustrating the same point might also be given.

In the second part of this paper, the results of a detailed investigation of the action of bromine on tetramethylenedicarboxylic acid,

$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$ , are described, an investigation which was undertaken in the first instance in the hope of obtaining tetrene-

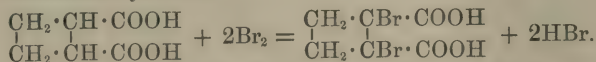
dicarboxylic acid,  $\begin{array}{c} \text{CH} \cdot \text{C} \cdot \text{COOH} \\ | \quad | \\ \text{CH} \cdot \text{C} \cdot \text{COOH} \end{array}$ , the study of which, in considera-

tion of the similarity of its constitution to that of phthalic acid, must have given very interesting results; but this acid could not be isolated. Nevertheless, many other substances were obtained which are of considerable interest.

When tetramethylenedicarboxylic anhydride is treated with excess of bromine in presence of phosphorus, substitution takes



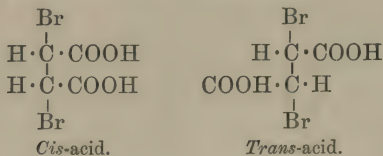
place, and the crystallised product of the reaction, after treatment with water, is found to consist principally of *cis*-dibromotetramethylenedicarboxylic acid,



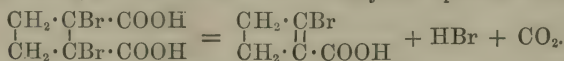
This acid melts at 202—205°, and when treated with acetic anhydride yields an anhydride (m. p. 104°); as this is reconverted into the original acid when dissolved in water, the latter must be the *cis*-dicarboxylic acid.

*Trans*-dibromotetramethylenedicarboxylic acid could not be obtained by heating the *cis*-acid in sealed tubes with concentrated hydrochloric or hydrobromic acid at 180°; the product from these experiments melted at 200—203°, and could not be distinguished from the *cis*-acid. The *trans*-acid is therefore either not formed in this way, or is very similar to the *cis*-acid in physical properties; the latter alternative is by no means improbable, as the *cis*- and *trans*-modifications of tetramethylenedicarboxylic acid are themselves so very similar that a careful examination of their chemical properties is necessary before they can be distinguished (Trans., this vol., 572).

It would be very remarkable if dibromotetramethylenedicarboxylic acid were found to exist in only one form, not only from the fact that the parent substance tetramethylenedicarboxylic acid itself exists in the *cis*- and *trans*-modifications, but also because succinic acid, which is similar to these acids in constitution, when treated with bromine, yields a mixture of stereoisomeric dibromo-acids.



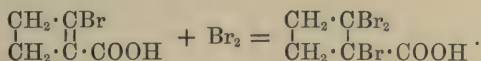
The study of the action of alkalis on dibromotetramethylenedicarboxylic acid has yielded very unexpected results, as, when this acid is treated with either strong or weak bases, such as potash, baryta, silver oxide, quinoline, or dimethylaniline, under various conditions, the principal product of the action, and indeed, in most cases the only product which could be isolated, was bromodihydrotetrenedicarboxylic acid, the formation of which may be represented thus



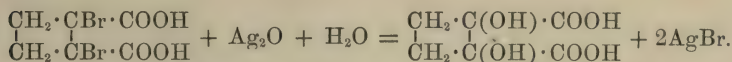
That the constitution of this new acid is represented as above, and not by the formula  $\begin{array}{c} \text{CH} : \text{CH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CBr} \cdot \text{COOH} \end{array}$ , is rendered very probable from an

examination of the properties of the acid. Its most remarkable property is its stability; when, for example, it is boiled for some time with strong potash (sp. gr. 1.3), or treated with silver oxide, it is not decomposed to any extent, and, on acidifying, the unchanged acid separates in crystals; this fact can only be explained on the assumption that the bromine-atom is attached to doubly bound carbon: in bromomaleic acid,  $\text{COOH} \cdot \text{CH} : \text{CBr} \cdot \text{COOH}$ , the bromine-atom is not removed by boiling with baryta water (Carius, *Annalen*, **149**, 264), whereas in saturated bromo-acids, as, for example, in the case of bromosuccinic acid,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{COOH}$ , the bromine-atom is readily eliminated by boiling with alkalis. The tendency of dibromotetramethylenedicarboxylic acid to be converted into bromodihydro-tetrenecarboxylic acid is very remarkable, this change taking place, with separation of iodine, when the aqueous solution of the dibromo-acid is warmed with potassium iodide, a change which it is difficult to represent by an equation.

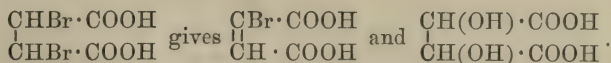
Bromodihydro-tetrenecarboxylic acid melts at  $121-122^\circ$ , and shows all the properties of an unsaturated acid; thus, it readily decolorises permanganate solution, and combines with bromine to form tribromotetramethylenedicarboxylic acid.



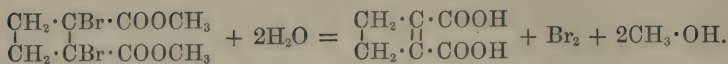
When silver oxide acts on an aqueous solution of dibromotetramethylenedicarboxylic acid, bromodihydro-tetrenecarboxylic acid is formed in considerable quantities, but the principal product of the action is a thick, syrupy acid, which, although it could not be obtained quite pure, is obviously dihydroxytetramethylenedicarboxylic acid,



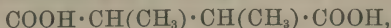
The reaction is in fact very similar to the formation of bromofumaric acid and tartaric acid from isodibromosuccinic acid under the same conditions.



The behaviour of methylic dibromotetramethylenedicarboxylate towards alkalis is, on the other hand, quite different from that of the free acid; when treated with alcoholic potash, for example, a curious action takes place; since bromine, and not, as was to be expected, hydrogen bromide is eliminated, dihydro-tetrenedicarboxylic acid being formed thus.



I have not been able to find a case exactly analogous to this, and illustrating the unstable nature of the bromine-atoms in this position, but it may be mentioned that dimethylsuccinic acid



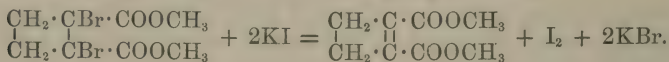
which, in constitution, closely resembles tetramethylenedicarboxylic acid, when treated with bromine and phosphorus, yields the anhy-

dride of pyrocinchonic acid  $\begin{array}{c} \text{CH}_3 \cdot \text{C} \cdot \text{CO} \\ || \\ \text{CH}_3 \cdot \text{C} \cdot \text{CO} \end{array} > \text{O}$ ; the intermediate dibromodimethylsuccinic acid which is probably formed, in the first instance, losing the two bromine atoms (Zelinsky, Krapivin *Berichte*, 22, 653).

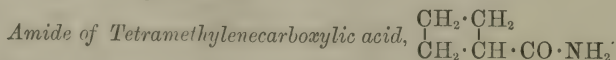
Dihydrotetrenedicarboxylic acid is sparingly soluble in cold water, melts at 178°, and when heated at 200° loses 1 mol. H<sub>2</sub>O, and is converted into an anhydride  $\begin{array}{c} \text{CH}_2 \cdot \text{C} \cdot \text{CO} \\ || \\ \text{CH}_2 \cdot \text{C} \cdot \text{CO} \end{array} > \text{O}$ , a resinous substance which could not be obtained in a crystalline form, and which dissolves in water with formation of a crystalline acid of the same empirical formula as dihydrotetrenedicarboxylic acid, from which, however, it differs in a very marked manner, notably in being excessively soluble in water. Whether these two acids are stereoisomeric or whether a change in the position of the double bond has taken place during the above treatment, has not yet been satisfactorily determined, owing to the small amount of material available for investigation.

The constitution of dihydrotetrenedicarboxylic acid is proved in the following way.

The methylic salt of this acid is formed quantitatively when methylic dibromotetramethylenedicarboxylate is digested in alcoholic solution with potassium iodide, iodine being liberated.



It is a beautifully crystalline substance which melts at 46°, and when exposed to bromine vapour is reconverted into methylic dibromotetramethylenedicarboxylate; it must therefore have the constitution represented above; dihydrotetrenedicarboxylic acid itself, on the other hand, may be exposed to bromine vapour for some days without change.



This has already been prepared by Freund and Gudeman (*Ber.*,



21, 2694), but not in a pure condition, as these chemists give the melting point  $138^{\circ}$ , whereas the pure amide melts at  $153^{\circ}$ .

In preparing large quantities of this amide, the following method was generally employed.

Pure tetramethylenecarboxylic chloride (10 grams) prepared as described in a previous paper (Trans., 1891, 59, 41) is added slowly through a dropping funnel to the strongest aqueous ammonia (100 c.c.), the whole being well cooled during the operation.

As each drop of the chloride comes in contact with the ammonia solution, a very vigorous action takes place, accompanied by volumes of white fumes, and, after about half has been added, the amide commences to separate in glistening plates which ultimately quite fill the liquid. The crystals are collected by means of the pump, washed once or twice with strong ammonia solution, dried on a porous plate in the air, and, if necessary, recrystallised from ether, in which the substance is sparingly soluble.

The amide is thus obtained in the form of magnificent, silky plates, which, on analysis, gave the following results.\*

	Theory. $C_4H_7 \cdot CO \cdot NH_2$ .	Found.
C .....	60.60 per cent.	60.75 per cent.
H .....	9.09       ,,	9.30       ,,
N .....	14.15       ,,	14.30       ,,

The amide of tetramethylenecarboxylic acid melts at  $152$ — $153^{\circ}$ , and is very readily soluble in water and alcohol, but only sparingly in ether; when heated, it sublimes in iridescent plates, which are very like sublimed benzoic acid in appearance; it is volatile even at  $100^{\circ}$ , and cannot be dried in a water oven without loss.

\* Considerable difficulty was experienced in determining the nitrogen in this substance, as, when burnt in a stream of carbon dioxide in the manner usually adopted, the result was always much too high, in two cases the analysis indicating 20 per cent. of nitrogen.

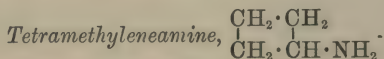
Obviously, during the combustion of this amide, very stable gases (ethylene?) are evolved, which pass away with the nitrogen into the eudiometer, and, in order to obviate this, an experiment was made, in which the tube was kept at a bright red heat and the combustion conducted slowly, but even then the result was 2 per cent. too high; the above nitrogen determination, which gave correct numbers, was carried out as follows.

The substance was digested with pure concentrated hydrochloric acid for five minutes, the solution then mixed with water and boiled until the odour of tetramethylenecarboxylic acid was imperceptible; the amount of ammonium chloride in the solution was then determined as ammonium platinochloride in the usual manner.

In several other cases it has been noticed that closed chain compounds are exceedingly difficult to analyse, and accurate results have only been obtained when the tube was kept very hot, and the combustion conducted throughout in a stream of oxygen.

It is very stable, as is illustrated by the fact that it was not entirely decomposed even after boiling for half an hour with strong potash, some of the unchanged amide separating in crystals on cooling; it is, however, very readily hydrolysed by boiling concentrated hydrochloric acid.

In preparing this amide in the manner described above, a considerable quantity remains in the ammoniacal mother liquors, but most of this may be recovered by repeated extraction with ether; any loss of valuable product is avoided by passing air through the aqueous solution until the bulk of the ammonia has been expelled, and then hydrolysing the dissolved amide by boiling with hydrochloric acid. The regenerated tetramethylenecarboxylic acid can be extracted with ether in the usual manner, and used for a subsequent operation.



This interesting substance is formed when the pure amide of tetramethylenecarboxylic acid is treated with bromine and potash, according to the well-known method devised by Hofmann (*Ber.*, **15**, 762); the details of the preparation are as follows.

Bromine (16.2 grams) is weighed out into a flask of about 500 c.c. capacity, and then the pure, finely-powdered amide (10 grams) is added in two or three portions with constant shaking, the whole gradually dissolving with evolution of very little heat.\*

At the end of two hours, potash (10 per cent.) is slowly added, the whole being well cooled during the operation; after a time, a reddish-brown, crystalline precipitate separates. On adding more alkali, very little rise of temperature takes place, but the precipitate becomes colourless, and doubtless consists of the bromamide of tetramethylenecarboxylic acid,  $\text{C}_4\text{H}_7 \cdot \text{CO} \cdot \text{NHBr}$ . On continuing to add strong potash (about 30—35 per cent.) in small quantities at a time with constant shaking, the bromamide gradually passes into solution; as now much heat is developed, the flask must be cooled from time to time by plunging it into water; when all the crystals have disappeared, the whole is distilled in a current of steam until the condensed water is no longer alkaline, and the distillate is then rendered slightly acid by the addition of hydrochloric acid, and evaporated to dryness.

The residue, which consists of a mixture of tetramethyleneamine hydrochloride and ammonium chloride, is extracted with absolute alcohol, the extract filtered from undissolved ammonium chloride, eva-

\* Freund and Gudeman (*loc. cit.*), using the impure amide, noticed the development of a considerable amount of heat.

porated to dryness, and the extraction with alcohol repeated. The crude hydrochloride obtained on evaporating the second extract is sufficiently pure for use in the preparation of hydroxytetramethylene, &c.

In order to isolate the base itself, the hydrochloride is transferred to a small retort, mixed with powdered potash, and distilled, the aqueous distillate is dehydrated with potash, and the oily base separated and fractioned; almost the whole of it distils between  $81^{\circ}$  and  $83^{\circ}$ , and, on refractionation, boils constantly at  $82^{\circ}$ .

On analysis the following numbers were obtained.

	Theory. $C_4H_9N$ .	Found.	
		I.	II.
C .....	67.60 per cent.	67.25	67.13 per cent.
H .....	12.67 "	12.60	12.58 "
N .....	19.72 "	19.58	— "

Tetramethyleneamine boils at  $82^{\circ}$ , and possesses a very pungent basic odour somewhat similar to that of isoamylamine; it absorbs carbon dioxide from the air, fumes strongly in contact with hydrogen chloride, and mixes with water with development of heat. The *hydrochloride*,  $C_4H_9N.HCl$ , was prepared by neutralising an aqueous solution of the base with hydrochloric acid, and evaporating to dryness. It crystallises from alcohol, in which it is readily soluble, in long, striated, prismatic needles, closely resembling crystals of ammonium chloride in appearance, and very readily soluble in water. The results of analysis gave

	Theory. $C_4H_9N.HCl$ .	Found.
Cl.....	33.02 per cent.	33.24 per cent.

On adding platinic chloride to a strong solution of the hydrochloride, the *platinochloride*,  $(C_4H_9N)_2H_2PtCl_6$ , is obtained as a deep yellow, crystalline precipitate, which dissolves readily in hot water, and separates on cooling in groups of deep orange octahedra. For analysis, the salt was dried at  $100^{\circ}$ .

	Theory. $(C_4H_9N)_2H_2PtCl_6$ .	Found.	
		I.	II.
Pt.....	34.87 per cent.	34.79	34.82 per cent.

This salt is rather sparingly soluble in cold water; when heated in a capillary tube, it begins to darken at  $200^{\circ}$ , and becomes quite black at  $210$ — $215^{\circ}$ .



The hydrochloride of tetramethyleneamine reacts readily with silver nitrite, evolving nitrogen and forming hydroxytetramethylene,

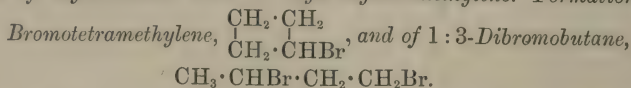


fortunately the reaction takes place with the formation of traces only of bye-products, and the yield of the hydroxy-compound obtained is, therefore, very good. The experiment was conducted as follows:—Crude tetramethyleneamine hydrochloride (20 grams), which had been freed from ammonium chloride by treatment with alcohol, as explained on p. 959, was dissolved in water (80 c.c.), and to the well-cooled solution a slight excess of freshly precipitated silver nitrite (prepared from 40 grams of silver nitrate), added in small quantities at a time. Effervescence soon began, and after remaining for one hour at the ordinary temperature the whole was heated on a water bath for a few minutes, until the vigorous evolution of gas had almost ceased. The product was then well cooled, mixed with anhydrous potassium carbonate, and extracted five times with pure ether; the ethereal solution was dried over anhydrous potassium carbonate, filtered, and the ether very slowly distilled off; a rectifying column being used so as to obviate, as far as possible, loss of the hydroxy-derivative by evaporation. The residual, almost colourless, oil (12 grams), after twice fractioning, boiled constantly at  $123^{\circ}$ , and gave the following results on analysis.

	Theory. $C_4H_7OH$ .	Found.	
		I.	II.
C .....	66·66 per cent.	66·52	66·41 per cent.
H .....	11·11 „	11·10	11·23 „

Hydroxytetramethylene is a colourless oil, which smells like butylic alcohol; it is readily soluble in water, and dissolves sodium with evolution of hydrogen and formation of a white sodium compound.

*Action of Hydrobromic acid on Hydroxytetramethylene. Formation of*



Having thus obtained hydroxytetramethylene, the next point was to investigate its behaviour with the halogen acids, in order, if possible, to prepare halogen derivatives of the hydrocarbon; the first experiments instituted were with hydrobromic acid.

Hydroxytetramethylene dissolves in fuming hydrobromic acid (saturated at about  $10^{\circ}$ ), with slight development of heat; as, however, little action appeared to take place in the cold, a large excess of the acid was added, and the whole heated to boiling in a flask, into the neck of which a reflux condenser had been ground. During the operation, a heavy oil separated on the surface of the liquid; but as the action continued and the hydrobromic acid became weak, the oil sank; after

heating for an hour, the product was poured into water, the heavy, brownish oil extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, and the ether evaporated. The residual oil was then repeatedly fractioned, and thus readily separated into two fractions, boiling at 102—104° and 173—174° (737 mm.) respectively; of these, the latter was present in by far the larger quantity. The substance boiling at 102—104° is evidently bromotetramethylene, as is shown by the following analyses.

	Theory. $C_4H_7Br$ .	Found.	
		I.	II.
C .....	35·55 per cent.	35·02	— per cent.
H .....	5·19 „	5·06	— „
Br .....	59·26 „	58·77	58·85 „

Bromotetramethylene is a colourless oil, which boils at about 104° (760 mm.); it is specifically heavier than water, and has an odour which can scarcely be distinguished from that of isobutylic or isoamyl bromide.

The substance boiling at 173—174° (737 mm.) is a very heavy oil, possessing in a marked degree the odour of trimethylene bromide; it gave, on analysis, the following numbers.

	Theory. $C_4H_8Br_2$ .	Found.	
		I.	II.
C .....	22·22 per cent.	22·00	— per cent.
H .....	3·71 „	3·70	— „
Br .....	74·07 „	74·32	74·21 „

These analyses show that this substance must be a dibromobutane, and its formation proves that, under the conditions of the experiment, the tetramethylene ring in bromotetramethylene has been split, addition of hydrogen bromide simultaneously taking place. As explained in the introduction, this dibromobutane is different from any of the known isomerides; and experiment proved that it is identical with the 1 : 3-dibromobutane, which is obtained when 1 : 3-dihydroxybutane,  $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot OH$ , is treated with hydrobromic acid (see next section).

*Preparation of 1 : 3-Dibromobutane,  $CH_3 \cdot CHBr \cdot CH_2 \cdot CH_2Br$ .*

This new substance was prepared in order to ascertain whether it was identical with the dibromobutane obtained by the action of hydrobromic acid on hydroxytetramethylene, as described in the last section, and the method employed was briefly as follows.\*

\* Compare Orndorff and Newbury, *Monatshefte für Chemie*, 13, 516.

Aldehyde (200 grams) was mixed with an equal volume of water, and then a strong solution of potassium carbonate (12 grams) added drop by drop, the whole being kept at  $0^{\circ}$  during the addition, which extended over about two hours; after standing for two days at the ordinary temperature, the mixture was neutralised with hydrochloric acid, extracted three times with ether, and the ethereal solution evaporated.

In order to convert the residue, which consisted of crude aldol (98 grams), into the corresponding 1 : 3-dihydroxybutane, it was dissolved in water (1 litre), and reduced in flat, porcelain basins with nearly twice the calculated quantity of  $2\frac{1}{2}$  per cent. sodium amalgam, the solution being kept neutral by the constant addition of small quantities of dilute hydrochloric acid, a rapid stream of carbon dioxide being also passed through the liquid, to prevent the accidental accumulation of any large quantity of alkali arising from rapid decomposition of the amalgam.

During the reduction, a sticky substance separated, and the solution also acquired a very penetrating and irritating odour, due possibly to the formation of crotonaldehyde; in order to remove these bye-products, the solution was filtered, and extracted with a small quantity of ether. The filtrate was then slowly concentrated to about 250 c.c. in a flask connected with a long, rectifying column, and the residue saturated with hydrogen bromide, without cooling, loss being prevented by using a reflux apparatus.

After 24 hours, the product was diluted with twice its volume of water, extracted five times with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, and the ether distilled off; the residual dark brown oil was then twice fractionated, and yielded 40 grams of 1 : 3-dibromobutane boiling at  $172-175^{\circ}$ , of which the greater portion passed over between  $173^{\circ}$  and  $174^{\circ}$ . Analysis—

	Theory.	Found.	
	$C_4H_8Br_2$ .	I.	II.
Br .....	74.07 per cent.	73.52	73.67 per cent.

The 1 : 3-dibromobutane obtained in this way boiled at the same temperature, and showed all the properties of the substance obtained by treating hydroxytetramethylene with hydrobromic acid, so that there can be no doubt the two products are identical.

I have to thank Messrs. G. H. Cross and J. N. Goldsmith, students in the Owens College, for help in carrying out these experiments.





This substance was prepared by the action of phosphorous pentachloride at moderate temperatures on hydroxytetramethylene, and not by heating this hydroxy-derivative with hydrochloric acid, as it appeared possible that, in the latter case, the chlorotetramethylene formed might be further acted on by the halogen acid with formation of dichlorobutane (see previous section).

Pure hydroxytetramethylene (11 grams) was placed in a flask fitted with a reflux condenser, and pure phosphorous pentachloride (35 grams) gradually introduced in small portions at a time; each successive quantity being allowed to entirely disappear before any more was added; the action, which is very vigorous and accompanied by the evolution of torrents of hydrogen chloride, was moderated by cooling the flask with ice-cold water; at the close, however, the temperature was allowed to rise to 60°.

The product was slowly fractioned, everything which passed over below 105° being collected,\* the distillate was agitated with water to decompose the phosphorous oxychloride which it contained, and the supernatant oily layer separated, dried over calcium chloride and fractionated; almost the whole of it (11.5 grams) passed over between 83° and 87°.

After refractionation, a colourless oil boiling constantly at 85° and specifically lighter than water, was obtained. On analysis it gave the following results.

	Theory. $\text{C}_4\text{H}_7\text{Cl}$ .	Found.
C .....	53.10 per cent.	53.07 per cent.
H .....	7.74     ,,	7.53     ,,
Cl .....	39.16     ,,	38.73     ,,

Chlorotetramethylene possesses a not disagreeable odour, very similar to that of isoamyl chloride.



In order to prepare this substance, chlorotetramethylene (8 grams) was heated with finely powdered potassium iodide (18 grams) and methylic alcohol (20 c.c.) in a sealed tube at 120—125° for five hours; the product, which was discoloured by iodine, was mixed with water, and the heavy oil which separated extracted with ether; the ethereal solution, washed with dilute sodium hydrogen sulphite, was dried over calcium chloride, evaporated, and the residue carefully fractioned.

\* On decomposing the residue with water, a very small quantity of oil separates; this was neglected.

It was then found that the oil contained about 50 per cent. of unchanged chlorotetramethylene; after this had passed over, the thermometer rose rapidly to  $130^{\circ}$ , between which temperature and  $140^{\circ}$  the remainder distilled as a colourless oil; on refractionation, it boiled almost constantly at  $138^{\circ}$ , and gave the following results on analysis.

	Theory. $C_4H_7I$ .	Found.
C .....	26.37 per cent.	26.85 per cent.
H .....	3.85     ,,	4.05     ,,
I .....	69.78     ,,	69.22     ,,

Iodotetramethylene is a colourless, heavy oil, which in its properties shows the greatest resemblance to isobutylic or isoamylic iodide; its odour can scarcely be distinguished from that of the latter, and, when exposed to light, it quickly turns brown owing to separation of iodine. It is readily reduced by zinc dust and hydrochloric acid with formation of a very volatile hydrocarbon, which is probably tetramethylene; unfortunately the amount of material at my disposal was too small to allow of the systematic examination of this reaction.

*Action of Quinoline on Iodotetramethylene.*—This action (compare Baeyer, *Annalen*, 278, 107) was investigated with the view of obtaining the unsaturated hydrocarbon dihydrotetrene,  $\begin{array}{c} CH_2 \cdot CH \\ | \quad || \\ CH_2 \cdot CH \end{array}$ , as explained in the introduction, but the results were not very satisfactory.

Iodotetramethylene (8 grams) was mixed with pure quinoline (15 grams) and the whole heated in a sealed tube at  $180^{\circ}$  for two hours; the product was then distilled from the tube, every precaution being taken to avoid loss of the volatile hydrocarbon by cooling the condenser and the receiver with a freezing mixture.

In this way, a small quantity of a colourless oil was obtained which boiled between  $30^{\circ}$  and  $45^{\circ}$ , and contained halogen; after heating in a small sealed tube with sodium and refractioning, the greater portion distilled between  $33^{\circ}$  and  $35^{\circ}$ , but it was not quite free from halogen. This substance is instantly oxidised by potassium permanganate and decolorises bromine; on analysis it gave numbers agreeing only approximately with the formula  $C_4H_6$ , owing not only to the presence of traces of halogen, but especially to the great difficulties attending the analysis of a hydrocarbon of this low boiling point.

*Dibromotetramethylenedicarboxylic acid*,  $\begin{array}{c} CH_2 \cdot CBr \cdot COOH \\ | \quad | \\ CH_2 \cdot CBr \cdot COOH \end{array}$

This acid is produced when the anhydride of tetramethylenedicarboxylic acid (this vol., 581) is treated with a large excess

of bromine and amorphous phosphorus, according to the Hell-Volhard-Zelinsky method.

Tetramethylenedicarboxylic anhydride (10 grams) is ground up in a mortar with amorphous phosphorus (3 grams), transferred to a flask, into the neck of which a condensing tube has been ground, and *dry* bromine (70 grams) then gradually added, the very vigorous action which takes place being moderated from time to time by cooling with water. On heating the mixture on a water bath, torrents of hydrogen bromide are evolved during the first hour; the action then slackens considerably, and at the end of six hours, a second quantity of phosphorus (3 grams) and bromine (70 grams) is added, and the heating continued for about 15 hours; air is then blown through the mass in order to remove excess of bromine, and the dark-coloured liquid residue, which on cooling frequently deposits crystals of phosphorus pentabromide, is decomposed cautiously by means of ice-cold water. After standing some time, the thick, dark brown product is extracted with ether, the ethereal solution, well washed with water containing a little sodium hydrogen sulphite, dried over calcium chloride, the ether distilled off, and the residual oil fractionated under reduced pressure (70 mm.).

The mass froths a good deal at first, and a considerable quantity of water distils over; the thermometer then rises rapidly, the greater portion distilling between 185 and 190° as an almost colourless oil, which solidifies in the receiver; a good deal of a dark brown residue is, however, left behind in the distilling flask.

The distillate is ground up and digested with sufficient hydrobromic acid (sp. gr. 1.49) to dissolve it, the solution filtered through glass wool and allowed to cool slowly; the mass of glistening crystals which separates is collected, washed with hydrobromic acid, drained on a porous plate, and recrystallised from the same solvent. The purified substance, after drying first over sticks of potash in a vacuum, and then at 100°, gave the following results on analysis.

	Found.		Theory. $C_6H_6Br_2O_4$ .
	I.	II.	
C .....	24.10	24.05 per cent.	23.84 per cent.
H .....	2.10	2.20     ,,	1.99     ,,
Br .....	52.71	—     ,,	52.98     ,,

When rapidly heated in a capillary tube, dibromotetramethylenedicarboxylic acid melts at about 202—205° with evolution of gas, probably due to the formation of its anhydride; it dissolves readily in alcohol or ether, and also in boiling hydrobromic acid, but is only sparingly soluble in the latter solvent in the cold. It is remarkable



that it is readily soluble in water; a strong, hot aqueous solution, on cooling, deposits the substance in beautiful glistening plates.

A moderately concentrated aqueous solution of this acid gives, with silver nitrate, a copious crystalline precipitate of a silver salt, which contains no silver bromide, as it is completely dissolved by dilute nitric acid. On boiling, however, decomposition sets in with separation of silver bromide in abundance.



Considerable quantities of this methylic salt were necessary for many of the experiments described in this paper, and in the first instance it was prepared from the pure dibromo-acid by treating it with methylic alcohol and hydrogen chloride in the usual way; ultimately, however, it was found that the best method of preparation was the following.

The crude product of the action of bromine and phosphorus on tetramethylenedicarboxylic anhydride (from which the excess of bromine had been removed by blowing in air, as described on p. 966), was poured in a thin stream, and without cooling, into a large excess of methylic alcohol; after the vigorous action had subsided, and the product cooled down, water was added, and the methylic salt extracted twice with ether. The ethereal solution was well washed with dilute sodium carbonate, dried over calcium chloride, the ether evaporated, and the residual dark brown oil fractionally distilled under reduced pressure (50 mm.).

With the exception of a small quantity of a substance of low boiling point, nearly the whole of the oil distilled between 180° and 205°, undergoing slight decomposition and evolving some hydrogen bromide; on redistilling, two principal fractions were obtained boiling at 185—195° and 195—200° (50 mm.) respectively. Both of these, after 14 days, deposited hard, prismatic crystals, which were separated from the oil by filtration through glass wool, left in contact with porous porcelain until quite dry and colourless, ground up, and then recrystallised twice from boiling light petroleum (b. p. 60—70°); in this way the methylic salt was obtained in magnificent, colourless prisms, which on analysis gave the following result.

	Found.	Theory. $\text{C}_4\text{H}_4\text{Br}_2(\text{COOCH}_3)_2$
C .....	29.21 per cent.	29.09 per cent.
H .....	3.30 „	3.03 „
Br .....	48.48 „	48.48 „

Methylic dibromotetramethylenedicarboxylate melts at 88—89°,

and is readily soluble in alcohol, chloroform, benzene, and hot, light petroleum, but only sparingly so in the latter solvent in the cold. It separates from dilute methylic alcohol in colourless groups of glistening, feathery crystals.

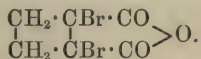
The oily mother liquor which was separated from the crystals, as explained above, was refractioned, and in this way a further, though small, quantity of crystalline methylic salt was obtained. After separating this, and again refractioning the mother liquor, no further crystallisation took place, even after the oil had been left for months in contact with a crystal of the methylic salt; analyses of two samples of this oil boiling at 190—195° and 195—200° (50 mm.) respectively, gave the following results.

	Found.		Theory.
	I.	II.	$C_4H_4Br_2(COOCH_3)_2$ .
Br. ....	46·30	47·10 per cent.	48·48 per cent.

It is possible that this product contains some impurity which retards crystallisation. As the analysis, however, seems to show that it can contain, at the most, only traces of such impurity, and as this would hardly prevent the separation of a substance characterised, like the methylic salt, by great facility for crystallising, it is possible that the liquid methylic salt is a stereoisomeride of the crystalline salt.

That there is a considerable difference between the solid and liquid methylic salt is shown clearly in their behaviour with potash (see p. 973).

*Anhydride of Dibromotetramethylenedicarboxylic acid,*



It has been shown in a previous communication (this vol., 572) that tetramethylenedicarboxylic acid [1:2] exists in two well-defined *cis*- and *trans*-modifications, and it might be supposed that its dibromoderivative would show the same behaviour. In order to investigate this point, it was necessary, in the first place, to prepare the anhydride of this acid, which was ultimately accomplished in the following way. Nearly pure dibromotetramethylenedicarboxylic acid (m. p. 185—190°) was distilled under a pressure of 40 mm., when almost the whole of it passed over at 180—185°, and solidified on cooling to a hard crystalline cake; this was dissolved in freshly distilled acetic anhydride, the solution boiled for five minutes in a reflux apparatus, and then placed over potash in a vacuum dessicator. As the excess of acetic anhydride evaporated, beautiful, colourless, prismatic

crystals separated; these were collected, washed with acetic anhydride, and dried over potash and sulphuric acid in a vacuum; they gave the following result on analysis.

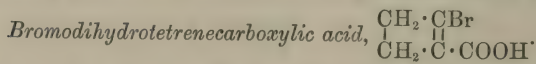
	Found.	Theory. C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub> O <sub>3</sub> .
C .....	25·21 per cent.	25·31 per cent.
H .....	1·72     ,,	1·41     ,,
Br .....	56·43     ,,	56·33     ,,

Dibromotetramethylenedicarboxylic anhydride melts at 103—104°, and is readily soluble in alcohol, ether, benzene, and boiling light petroleum (b. p. 100°), but only sparingly in the latter in the cold. In contact with moisture, it is readily converted into the acid from which it was derived; some of the powdered substance which was left exposed to the air for a few days had almost entirely changed, and then melted at about 180°. The anhydride dissolves readily in warm water, and the solution on cooling deposits pure dibromotetramethylenedicarboxylic acid in glistening crystals (m. p. 204—205°). This acid is therefore the *cis*-modification.

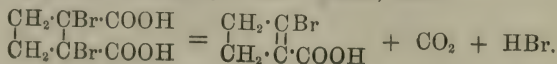
In order to determine whether the corresponding *trans*-modification existed, some of the pure anhydride was dissolved in warm hydrobromic acid solution (sp. gr. 1·49) and heated in a sealed tube at 190—200° for two hours. On cooling, the tube was found to be filled with glistening crystals, very little discoloration and no charring having taken place; these crystals were collected and recrystallised from hydrobromic acid; they melted then at about 200°, and were exactly similar in appearance to the original *cis*-acid.

It appears, therefore, that the *trans*-modification of dibromotetramethylenedicarboxylic acid does not exist: unless indeed it is so similar in properties to the *cis* form that it could only be identified on very prolonged investigation.

*Action of Alkalis on Dibromotetramethylenedicarboxylic acid.*



As explained in the introduction, these experiments were instituted with the object of obtaining pyrenedicarboxylic acid,  $\begin{array}{c} \text{CH} : \text{C} \cdot \text{COOH} \\ | \\ \text{CH} : \text{C} \cdot \text{COOH} \end{array}$ ; but, although the conditions were varied as far as possible, this acid could never be isolated; the reaction proceeded in all cases in the same way, carbon dioxide and hydrogen bromide being eliminated, and bromodihydropyrenedicarboxylic acid formed, thus:





1. *Experiments with Barium Hydroxide.*—Pure dibromotetramethylenedicarboxylic acid (about 5 grams) was dissolved in a little warm water and the solution mixed with a large excess of hot, strong barium hydroxide; this caused the separation of a white, glistening, crystalline precipitate which was very sparingly soluble even in boiling water, and probably consisted of the barium salt of the dibromo-acid; on continued boiling, however, this was gradually decomposed and passed into solution, much hydrogen bromide being eliminated, as was proved by testing the solution with silver nitrate. After filtering from a small quantity of insoluble matter, carbon dioxide was passed through the boiling liquid to precipitate the excess of baryta, and the whole filtered hot; the filtrate, on being evaporated to a small bulk and allowed to cool, deposited colourless crystals which, after recrystallisation from water and drying at  $100^{\circ}$ , gave the following results on analysis.

	Found.		Theory. $C_{10}H_8Br_2O_4Ba$ .
	I.	II.	
Ba . . . . .	28.03	28.02 per cent.	28.02 per cent.
Br* . . . . .	33.01	— „	32.72 „

On drying at  $100^{\circ}$ , the air-dry glistening crystals become opaque and lose 9.77 per cent. in weight, which appears to show that the freshly prepared salt has the composition,  $C_{10}H_8Br_2O_4Ba + 3H_2O$  (containing 9.96 per cent.  $H_2O$ ). This water of crystallisation is gradually given off, when the crystals are left exposed over sulphuric acid in a dessicator for a long time.

The barium salt is sparingly soluble in cold, but readily in hot water: on adding hydrochloric acid to the hot solution, and allowing it to cool slowly, bromodihydrotetrenecarboxylic acid separates in colourless needles which, after recrystallising from water, gave the following results on analysis.

	Found.	Theory. $C_4H_4BrCOOH$ .
C . . . . .	34.20 per cent.	33.90 per cent.
H . . . . .	2.97 „	2.83 „
Br . . . . .	45.23 „	45.18 „

The acid melts at  $121$ — $122^{\circ}$ , and is sparingly soluble in cold water, readily in hot water, chloroform, alcohol, ether, benzene, and hot light petroleum; it is best crystallised from hot water or light petroleum. That it is an unsaturated acid is shown firstly by the behaviour of the cold solution of its sodium salt with a drop of permanganate, which it instantaneously decolorises, and, secondly, by

\* In order to determine the bromine in this salt, it was found necessary to heat the substance with fuming nitric acid and silver nitrate for 5 hours at  $200$ — $220^{\circ}$ .

its conversion into tribromotetramethylenecarboxylic acid when treated with bromine.

The bromine-atom in bromodihydrotetrenecarboxylic acid is very firmly bound, and is only very slowly eliminated by boiling with silver hydroxide, potash, quinoline, and other alkalies; the acid dissolves also in fuming nitric acid, and the solution may be warmed almost to the boiling point without elimination of bromine; ultimately, however, vigorous oxidation sets in, and the acid is rapidly decomposed.

*Action of Potash on Dibromotetramethylenedicarboxylic acid.*—If this acid be digested with excess of potash instead of with baryta, and the solution acidified and extracted with ether, a yellow, semi-solid acid is obtained on evaporating the ethereal solution. If left in contact with porous porcelain, this becomes quite hard and almost colourless, and, after recrystallisation from water with the aid of animal charcoal, yields colourless crystals of bromodihydrotetrenecarboxylic acid. It melted at  $122^{\circ}$ , and on analysis gave the following result.

	Found.	Theory. $C_5H_5BrO_2$ .
Br.....	45.32 per cent.	45.18 per cent.

Many experiments were then made with the object of eliminating hydrogen bromide from this monobromo-acid by boiling with aqueous and alcoholic solutions of potash of various degrees of concentration, but in no case could the desired tetrenecarboxylic acid,  $\begin{array}{c} CH:CH \\ | \quad | \\ CH:C \cdot COOH \end{array}$ , be isolated.

*Action of Quinoline and of Dimethylaniline on Dibromotetramethylenedicarboxylic Anhydride.*—When this anhydride is gently heated with quinoline, a vigorous action sets in, and a good deal of charring takes place; on examining the product, the only crystalline substance which could be isolated was found to be bromodihydrotetrenecarboxylic acid melting at  $122^{\circ}$ , showing that the quinoline had acted much in the same way as the baryta water and the potash, 1 mol. of hydrogen bromide only being eliminated.

A similar result was obtained with dimethylaniline, but the action proceeded much more smoothly, and with little charring; 0.5 gram of the pure anhydride was dissolved in 10 grams of pure dimethylaniline, and the solution heated gently until the vigorous action which soon sets in had subsided; the temperature was then raised to the boiling point of the liquid for a few seconds.

The product was then digested with alcoholic potash for 10 minutes, the dimethylaniline removed by distillation in steam, the alkaline solution filtered, acidified and extracted with ether; the residue left on distilling the ether gave colourless needles, which when crystallised

from water melted at  $122^{\circ}$ , and showed all the properties of bromodihydrotetrenecarboxylic acid.

*Action of Silver Oxide on Dibromotetramethylenedicarboxylic acid.*—As it was not found possible to remove all the bromine from this acid by means of baryta or potash, experiments on the action of silver oxide were instituted.

About 5 grams of the pure dibromo-acid was dissolved in half a litre of water, and freshly prepared silver oxide was added in small quantities to the solution heated nearly to boiling, until, after standing for some time and filtering, the solution was found to contain a considerable quantity of silver on testing it with hydrochloric acid; when this point was reached it was found to be disadvantageous to warm any further, otherwise the organic silver salt present decomposes with deposition of silver. A stream of hydrogen sulphide was then passed through the warm filtered liquid until the whole of the silver had been precipitated, and the clear solution was evaporated to a small bulk and allowed to stand over sulphuric acid in a vacuum. After two days, the crystalline precipitate which had separated was collected and recrystallised from water; it then melted at  $122^{\circ}$  and consisted of bromodihydrotetrenecarboxylic acid, as the following analysis shows.

	Found.	Theory. $C_4H_4Br \cdot COOH$ .
Br .....	45.41 per cent.	45.18 per cent.

The dark coloured filtrate from these crystals was digested with carefully purified animal charcoal and allowed to evaporate to dryness over sulphuric acid in a vacuum, the resulting syrupy mass was then rubbed up with a little water, a few crystals which remained undissolved removed by filtration, and the filtrate again allowed to evaporate, the treatment with cold water being repeated until the solution contained only traces of bromine.

The pale yellow syrup ultimately obtained on evaporation showed no signs of crystallising even after standing in a dessicator for a fortnight; when heated at  $100^{\circ}$ , it lost water and yielded a brittle, transparent resin which on analysis gave the following results.

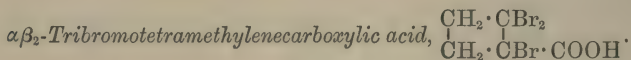
	Found.		Theory.
	<div style="display: flex; justify-content: space-around;"> <span>I.</span> <span>II.</span> </div>		$CH_2 \cdot C(OH) \cdot COOH$ $CH_2 \cdot C(OH) \cdot COOH$
C .....	40.41	40.46 per cent.	40.91 per cent.
H .....	4.34	4.51     „	4.55     „

As these analyses were carried out with the product from two distinct experiments, it seems probable that this substance is slightly impure dihydroxytetramethylenedicarboxylic acid, the formation of which was to be expected from the conditions of the experiment:



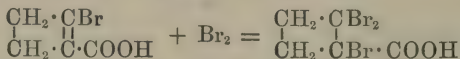
and the behaviour of the acid favours this view. When heated, it readily chars, giving off a strong smell of burnt sugar; sulphuric acid also quickly chars the acid when the mixture is gently warmed; the acid is very readily soluble in water and reduces ammoniacal silver solution rapidly at 80—100°, in these respects behaving very like tartaric acid. On the other hand, it does not appear to form a sparingly soluble potassium salt.

*Action of Potash on liquid Methylic Dibromotetramethylenedicarboxylate.*—A quantity of this substance which boiled constantly at 190—195° (50 mm.) was digested with alcoholic potash, the product diluted with water, evaporated till free from alcohol, acidified and extracted with ether. The residue left on distilling off the ether, when repeatedly recrystallised from water with the aid of animal charcoal, yielded considerable quantities of bromodihydrotetrenecarboxylic acid, also a mixture of acids melting about 150°, which were not further investigated, and traces only of dihydrotetrendicarboxylic acid. This difference in the behaviour of the liquid and solid methylic salt towards potash is remarkable, and shows that there must be a considerable difference in their constitutions.



A solution of bromodihydrotetrenecarboxylic acid in chloroform is only very slowly attacked by bromine. Addition, however, readily takes place if the finely divided acid is left under a bell-jar in contact with *dry*\* bromine vapour, the reaction proceeding quantitatively as is shown by the following experiment.

0.1074 gram of substance left in contact with dry bromine vapour during 24 hours yielded a red liquid, which, after standing over potash in a vacuum dessicator until the excess of bromine had evaporated, became quite hard and almost colourless, and weighed 0.2044 gram, an increase of 0.0970 gram. On the assumption that addition takes place according to the equation

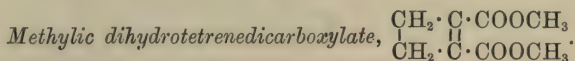


the increase should have been 0.0971 gram. The product was analysed by heating it with fuming nitric acid and silver nitrate at 210° for 5 hours, and gave the following results agreeing with the formula of tribromotetramethylenecarboxylic acid.

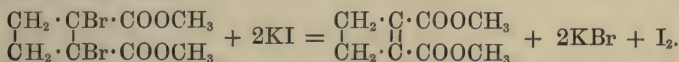
\* If the bromine vapour be moist, oxidation sets in, and an uninviting sticky substance is formed.

	Found.	Theory. $C_4H_4Br_3 \cdot COOH$ .
Br.....	70.96 per cent.	71.21 per cent.

Tribromotetramethylenecarboxylic acid is readily soluble in benzene and alcohol, sparingly in water and light petroleum; but attempts to recrystallise the substance were unsuccessful, as it readily decomposes when warmed with solvents.



This beautiful substance is formed when methylic dibromotetramethylenedicarboxylate is digested in alcoholic solution with potassium iodide, thus



Pure methylic dibromotetramethylenedicarboxylate (2 grams) is dissolved in absolute alcohol (20 c.c.) finely powdered potassium iodide (4 grams) added, and the mixture heated to boiling in a flask connected with a reflux apparatus; the solution very soon begins to darken in colour owing to the separation of iodine, and after boiling for 2 hours the decomposition is complete. In order to isolate the product of the action, water is added, the dark oily mass extracted four times with ether, the ethereal solution washed with dilute sodium hydrogen sulphite until colourless, and then with water; after drying over calcium chloride, and evaporating, a thick colourless oil is obtained, which, on cooling, solidifies to a mass of crystals.

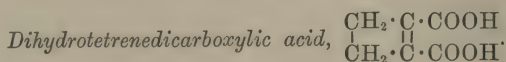
The crystalline mass after being left in contact with porous porcelain until quite free from oily mother liquor, was recrystallised twice from light petroleum (b. p. 50–60°), when magnificent glistening crystals were obtained. On analysis, these gave the following results.

	Found.		Theory.
	I.	II.	$C_4H_4(COOCH_3)_2$ .
C.....	56.14	56.21 per cent.	56.47 per cent.
H.....	5.93	5.95 „	5.88 „

*Methylic dihydrotetrenedicarboxylate* melts at 44–46° and is readily soluble in methylic or ethylic alcohols, ether, benzene, and hot light petroleum, but only sparingly in the latter solvent in the cold; it crystallises from most solvents with great facility.

A small quantity of the finely powdered substance was exposed under a bell glass to the vapour of dry bromine for 15 hours; after removal of the excess of bromine over potash in a vacuum, a colourless mass was left which crystallised in needles melting at 84–86°.

and showed all the properties of methylic dibromotetramethylenedicarboxylate; it was doubtless identical with the latter, but no analysis of the product could be made owing to the small amount of substance available.



In order to prepare this acid, the pure methylic salt was digested for 10 minutes with an excess of alcoholic potash, the solution of the potassium salt mixed with water, evaporated until free from alcohol, acidified and extracted at least 10 times with ether; the ethereal solution was then dried by calcium chloride, evaporated, and the residual almost colourless acid purified by recrystallisation from water. Analysis

	Found.		Theory.
	I.	II.	$\text{C}_4\text{H}_4(\text{COOH})_2$ .
C .....	50.49	50.60 per cent.	50.70 per cent.
H .....	4.15	4.25 „	4.23 „

Dihydrotetrenedicarboxylic acid crystallises from water in colourless needles which melt and decompose at about  $178^\circ$  forming the anhydride. It is readily soluble in hot water and alcohol, sparingly in cold water, benzene, or ether, and almost insoluble in light petroleum. It dissolves readily in dilute sodium carbonate, and the solution decolorises permanganate very rapidly, a proof that the acid is unsaturated.

When exposed to dry bromine vapour, it is either not acted on at all or action takes place with extreme slowness, which is rather remarkable as the methylic salt under the same conditions is readily converted into methylic dibromotetramethylenedicarboxylate. If a little of the acid be carefully heated in a test tube, water is given off at first, and the residue then rapidly decomposes, a carbonaceous mass being left: in this respect the acid differs widely from compounds of analogous constitution, such as fumaric acid or pyrocinchonic anhydride which distil without decomposition.

*Silver Salt*  $\text{C}_4\text{H}_4(\text{COOAg})_2$ .—This salt is obtained as a white amorphous precipitate on adding a large excess of silver nitrate to a warm, slightly alkaline, solution of the ammonium salt; it was collected, washed with warm water, dried over sulphuric acid in a vacuum and then at  $100^\circ$ , and analysed with the following result.

	Found.	Theory.
		$\text{C}_6\text{H}_4\text{Ag}_2\text{O}_4$ .
C .....	20.22 per cent.	20.22 per cent.
H .....	0.95 „	1.12 „
Ag .....	60.32 „	60.67 „



This silver salt is very sparingly soluble in water; when heated it decomposes all at once, yielding a very voluminous mass of silver, for which reason the above silver determination had to be carried out in the wet way.

*Hydrogen Silver Salt*,  $\text{COOH} \cdot \text{C}_4\text{H}_4 \cdot \text{COOAg}$ .—The warm mother liquors from the above salt, after two days, deposited magnificent, glistening needles of the hydrogen silver salt; these were collected, washed with water, dried over sulphuric acid in a vacuum and then at  $100^\circ$ , and analysed.

	Found.		Theory.
	I.	II.	$\text{C}_6\text{H}_5\text{AgO}_4$ .
Ag . . . .	42.94	43.12 per cent.	43.35 per cent.

It is remarkable that the corresponding dihydropentenedicarboxylic acid (p. 983) should give a similarly constituted hydrogen silver salt, and that both salts, when they have once crystallised, should be so sparingly soluble in water.

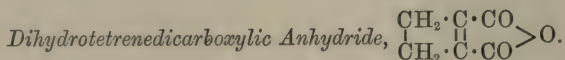
Dihydrotetrenedicarboxylic acid is also produced when methylic dibromotetramethylenedicarboxylate (p. 967) is treated with alcoholic potash, the action in this case being quite different from that which takes place when dibromotetramethylenedicarboxylic acid itself is heated with alkalis.

The pure methylic salt (5 grams) was dissolved in a little boiling alcohol, and a strong solution of potash (7 grams) in alcohol gradually added; a vigorous action took place, and in a short time the whole solidified to a crystalline mass.

On subsequently warming on a water bath, most of the crystals gradually disappeared, and the colour of the liquid changed to dark brown; after two hours' digestion in a reflux apparatus, water was added, the solution evaporated until free from alcohol, filtered, acidified, and extracted 10 times with ether; the ethereal solution was then dried over calcium chloride, filtered, and the ether slowly distilled off. During the distillation, and after the bulk of the ether had distilled over, crystals separated; these were collected, washed with a little ether to remove the dark-coloured mother liquor, and purified by recrystallisation from water with the aid of animal charcoal. The colourless crystals thus obtained melted at  $178^\circ$ , and consisted of pure dihydrotetrenedicarboxylic acid, as the following analysis shows.

	Found.		Theory.
			$\text{C}_4\text{H}_4(\text{COOH})_2$ .
C . . . . .	50.35	per cent.	50.70 per cent.
H . . . . .	4.31	„	4.23 „

This reaction does not afford a convenient means of preparing this acid, as the yield is not good, and the product is much more difficult to purify than that obtained from the pure methylic salt, as previously explained (p. 975).



In the first experiments made with the object of preparing this anhydride, the pure acid was digested with acetyl chloride and with acetic anhydride for one hour; endeavours to purify the dark-coloured product by distillation under reduced pressure (20 mm.) were fruitless, because as soon as the excess of acetic anhydride or acetyl chloride had passed over and the temperature rose above 150°, rapid decomposition set in, and the whole mass became quite black. When, however, the pure acid was heated in a test tube at 190—200°, vigorous effervescence took place, water was eliminated, and the action was complete in five minutes; the product, which on cooling set to a hard, transparent resin, was analysed, two distinct preparations giving the following numbers.

	Found.		Theory. $\text{C}_4\text{H}_4\text{C}_2\text{O}_3$ .
	I.	II.	
C .....	57.47	57.55 per cent.	58.06 per cent.
H .....	3.29	3.27 „	3.23 „

This substance is obviously the anhydride of dihydropentenedicarboxylic acid. It is a resinous substance, which melts in the steam oven, and could not be obtained in a crystalline form; when boiled with water, it melts and gradually dissolves, forming a clear solution, and this, if allowed to evaporate over sulphuric acid in a vacuum leaves a syrupy residue which, on long standing, deposits crystals.

In contact with porous porcelain, these crystals lose the adherent, syrupy mother liquor, and become quite colourless, but all attempts to recrystallise the substance failed; two distinct preparations were dried at 100°, and analysed with the following results.

	Found.		Theory. $\text{C}_4\text{H}_4(\text{COOH})_2$ .
	I.	II.	
C .....	50.63	50.59 per cent.	50.70 per cent.
H .....	4.10	4.25 „	4.23 „

This acid is, therefore, isomeric with dihydropentenedicarboxylic acid (m. p. 178°), and it differs from this in a most marked manner; it is, for example, excessively soluble in water and ether, and cannot be recrystallised, whereas the acid of melting point 178° is sparingly soluble in these solvents, and is remarkable for the great

facility with which it crystallises. Unfortunately the small quantity of material at my disposal made it impossible for me to further investigate this substance.

*Action of Potassium Iodide on Dibromotetramethylenedicarboxylic acid.  
Formation of Bromodihydrotetrenecarboxylic acid.*

The formation of methylic dihydrotetrenedicarboxylate by the action of potassium iodide on methylic dibromotetramethylenedicarboxylate made it interesting to determine whether dihydrotetrenedicarboxylic acid itself might be produced by treating the dibromo-acid with potassium iodide.

The pure dibromo-acid (2 grams) was mixed with a strong solution of potassium iodide (10 grams) and allowed to stand, when it was noticed that even in the cold the solution gradually acquired a yellow tint, due to liberation of iodine; at 100°, in a sealed tube, decomposition took place rapidly, and after two hours the liquid had become dark brown. On allowing the tube to remain over night in a cool place, crystals were deposited, and when the tube was opened a slight pressure was noticeable, due to carbon dioxide. The crystals were collected, washed with water, and recrystallised several times from this solvent, when they became colourless. The substance melted at 122°, and, on analysis, was found to consist of bromodihydrotetrenecarboxylic acid.

	Found.	Theory.
Br .....	44.95 per cent.	45.18 per cent.

It is remarkable that there should be such a difference between the behaviour of dibromotetramethylenedicarboxylic acid and that of its methylic salt, when treated with potassium iodide.

*The Owens College,  
Manchester.*





THE "CIS"— AND "TRANS"— MODIFICATION  
OF TETRAMETHYLENEDICARBOXYLIC ACID  
(1, 2) AND PENTAMETHYLENEDICARBOXYLIC  
ACID (1, 2).

BY

W. H. PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1894.]



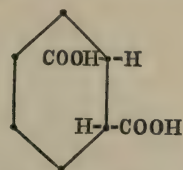


The 'cis-' and 'trans-' modification of tetramethylenedicarboxylic acid (1.2) and pentamethylenedicarboxylic acid (1.2).

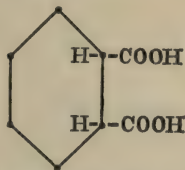
By W. H. PERKIN, Jun.

In the course of his interesting researches on the reduction of phthalic acid (*Annalen*, 258, 145; 269, 145), Baeyer has shown that hexahydrophthalic acid exists in two modifications, which differ very widely in their properties, and which he distinguishes by the prefixes "fumaroid" or "*trans*" and "maleinoid" or "*cis*."

Graphically, these two acids may be represented thus—



*Trans*- or fumaroid  
modification.



*Cis*- or maleinoid  
modification.

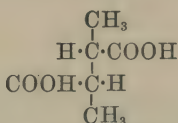
but it is not easy to clearly understand the different arrangement of the groups of atoms in these two formulæ unless models are used. The properties of the *trans*- and *cis*-hexahydrophthalic acids which have a direct bearing on the results described in this paper are the following.

The *trans*-acid (m. p. 215°) distils unchanged if quickly heated, but when kept at a temperature slightly above its melting point, water is eliminated, and the acid is partly converted into the anhydride of the *cis*-acid.

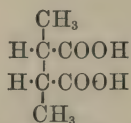
The *cis*-acid (m. p. 192°) is gradually decomposed at its melting point, yielding the anhydride, which melts at 32°, and when heated with hydrochloric acid at 180°, it is converted into the *trans*-acid.

One of the most interesting results obtained in the examination of these acids is the observation that the *trans*-acid, when heated with acetyl chloride, also yields an anhydride melting at  $140^{\circ}$ , which, at a temperature of  $210\text{--}220^{\circ}$ , is gradually converted into the anhydride of the *cis*-acid.

Baeyer points out the great similarity there is between these acids and the dimethylsuccinic acids, which also exist in two modifications—



*Trans*-modification.



*Cis*-modification.

These two modifications are convertible the one into the other, by the same methods as those used in the case of the hexahydrophthalic acids; both yield anhydrides, melting at  $87^{\circ}$  and  $38^{\circ}$  respectively, the former being converted into the latter by heating.

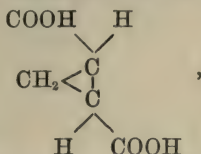
It is quite easy to understand from an examination of the models that the *cis*-acids should, like maleïc and succinic acids, yield anhydrides, but it is somewhat more difficult to explain the existence of the *trans*-anhydrides, especially when the fact is taken into account that it has not been found possible to produce an anhydride of fumaric acid.

However, as Baeyer carefully points out, the study of the molecule models of these *trans*-acids at once reveals the fact that the relative directions of the affinities holding the carboxyl groups are not by any means the same—the affinities in the case of fumaric acid being inclined at an angle of  $180^{\circ}$ , whereas in the case of the *trans*-hexahydrophthalic acid and *trans*-dimethylsuccinic acid the angle is approximately  $109^{\circ}$ .

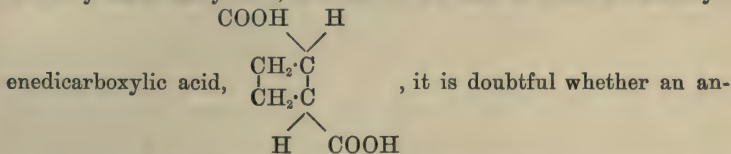
It may be assumed, therefore, that the reason why fumaric acid does not give an anhydride is because the distance between the two carboxyl groups is too great; in the case of *trans*-hexahydrophthalic acid and *trans*-dimethylsuccinic acid, the distance is far less, and the strain necessary to bring the two carboxyl groups together is not sufficient to prevent the formation of an anhydride; nevertheless, as the strain is still much greater than in the anhydrides of the *cis*-acids, it may be assumed that there is a tendency in the *trans*-anhydrides to change into the more stable *cis*-forms.

From considerations such as these, Baeyer concludes that the *trans*-modification of 1 : 2-pentamethylenedicarboxylic acid must also yield an anhydride, because the conditions of strain in this acid are almost exactly the same as in *trans*-hexahydrophthalic and *trans*-dimethyl-

succinic acids; he also states that it is clear, from the examination of the models, that *trans*-trimethylenedicarboxylic acid,



cannot yield an anhydride, whereas in the case of *trans*-tetramethyl-



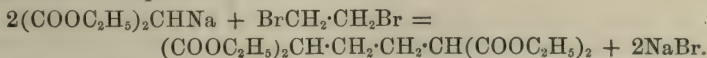
hydride could be formed or not. These theoretical deductions agree with the known facts as far as trimethylenedicarboxylic acid is concerned; the *trans*-modification of this acid does not give an anhydride, although the *cis*-modification does.

With regard to the intermediate tetramethylene- and pentamethylenedicarboxylic acids, the *cis*- and *trans*-modifications of these acids had not at that time been prepared; and, indeed, some preliminary experiments which I made with the object of obtaining two modifications of 1:2-tetramethylenedicarboxylic acid gave results which, I thought, pointed to the existence of only one form of this acid (compare *Ber.*, **26**, 2245).

This want of success was doubtless due to the very slight difference in the melting points of the two tetramethylene acids, as some time since, on again carefully experimenting on the subject, I found that both tetramethylene- and pentamethylene-dicarboxylic acids exist in well defined *cis*- and *trans*-modifications.

Tetramethylenedicarboxylic acid (m. p. 138°)\* has been described in a previous paper (*Trans.*, 1890, **57**, 18). It was prepared by the following series of reactions, which leave no doubt as to its constitution.

When ethylene dibromide acts on the sodium compound of ethylic malonate, ethylic trimethylenedicarboxylate is formed, together with small quantities of ethylic butanetetra-carboxylate, the latter resulting from the direct action of 1 mol. of ethylene bromide on 2 mols. of the sodium compound, thus—



This ethereal salt yields a disodium compound, which, when

\* The melting point, 130°, previously given, is too low.







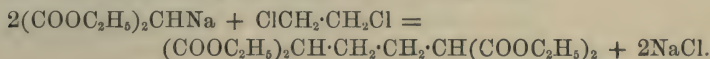




The results of this investigation show once again that it is not safe to attempt to deduce the configuration of stereoisomeric acids from their melting points or dissociation constants; the only sure method is to investigate the behaviour of the isomers when treated with acetyl chloride and with hydrochloric acid at a high temperature.

*Preparation of Ethylic Butanetetra-carboxylate,*  
 $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$ .

This substance is best obtained, as explained in the Introduction to this paper, by treating the sodium compound of ethylic malonate with ethylene chloride, the reaction proceeding thus—



The details of the preparation are as follows.

9.2 grams of sodium is dissolved in 120 c.c. of absolute alcohol, and the solution, when quite cold, transferred to a soda-water bottle, 64 grams of ethylic malonate and 21 grams of ethylene chloride added, and the whole mixed as thoroughly as possible by shaking, an operation rendered somewhat difficult on account of the separation of solid particles of the sodium compound of ethylic malonate, which sometimes cause the liquid to set to a jelly-like mass. The soda-water bottle is securely corked and tied down, and heated in a water bath at  $100^\circ$  for eight hours; usually four to six such bottles were heated at the same time. When cold, the alcoholic solution is carefully decanted from the cake of sodium chloride which has separated, and the alcohol distilled off on a water bath; the residue, together with that remaining in the bottles, is then mixed with sufficient water to dissolve the salt, and extracted three times with ether.

The ethereal solution is well washed with water, dried over calcium chloride, the ether distilled off, and the brownish, oily residue, which from four bottles weighs always about 220 grams, is fractioned under reduced pressure\* (40 mm.) until the thermometer, immersed in the boiling liquid, rises to  $150^\circ$ .

The colourless oil (125 grams) which passes over consists of a mixture of ethylic trimethylenedicarboxylate with unchanged ethylic malonate; the very dark coloured residue (70 grams) which remains in the distilling flask contains ethylic butanetetra-carboxylate. The distillate of low boiling point is now fractioned under the ordinary pressure, and the fraction  $180\text{--}225^\circ$  collected and used again in pre-

\* In this and in subsequent distillations, when the amount of liquid to be fractioned was not less than 50 c.c., the distillation flasks recommended by Claisen (*Annalen*, 277, 177) were found to be very useful, as, with these, there is much less risk of frothing over than when the ordinary fractioning flasks are used.



paring further quantities of ethylic butanetetracarboxylate, the operation being conducted in the same way as before, except that, as this fraction is assumed to contain only 50 per cent. of ethylic malonate, the relative quantities employed are 128 grams of oil, 9.2 grams of sodium, and 21 grams of ethylene chloride; the isolation and separation of the product into two fractions is carried out as before.

It is very remarkable that the yield of crude ethylic butanetetracarboxylate is now very much larger than in the first series of operations; from four bottles (in each of which 128 grams of recovered oil had been treated), no less than 440 grams of oil, boiling above  $150^{\circ}$  (40 mm.), was obtained, or at least double that resulting from the treatment of pure ethylic malonate; and it is also noticeable that the product obtained in the second preparation is not nearly so dark coloured, and is much more easily purified.

The crude ethylic butanetetracarboxylate is now submitted to fractional distillation under reduced pressure (40 mm.), not more than 100 grams being distilled at once; a small quantity of oil passes over below  $200^{\circ}$ , but the temperature rises rapidly to  $230^{\circ}$ , between which and  $250^{\circ}$  the principal portion distils as an almost colourless oil, a small quantity of a tarry mass remaining in the flask.

The distillate is once more fractioned, and the fraction  $230\text{--}250^{\circ}$  (40 mm.) collected for use in subsequent experiments; the amount obtained from 500 grams of crude oil boiling above  $150^{\circ}$  (40 mm.) is about 300—320 grams. That this oil is nearly pure ethylic butanetetracarboxylate is shown by the following analysis.

	Found.	Theory. $\text{C}_{16}\text{H}_{26}\text{O}_8$ .
C .....	55.21 per cent.	55.49 per cent.
H .....	7.67 „	7.51 „

Pure ethylic butanetetracarboxylate boils at  $240\text{--}245^{\circ}$  (50 mm.). The oil from the second preparation, boiling below  $150^{\circ}$  (40 mm.), is fractioned as before under ordinary pressure, and the portion boiling at  $180\text{--}225^{\circ}$  mixed with one-third of its weight of ethylic malonate, and again treated with sodium ethoxide and ethylene chloride, the quantities to be employed being calculated on the assumption that the mixture now contains 50 per cent. of ethylic malonate.

As the result of a number of experiments it was found that this method could be continued apparently indefinitely; after the first preparation, the yield of ethylic butanetetracarboxylate is always very good. This reaction is at present being carefully investigated with a view to affording some explanation of the remarkable series of decompositions which evidently take place.

1:1:2:2-Tetramethylenetetra-carboxylic acid,  $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{COOH})_2 \\ | \\ \text{CH}_2 \cdot \text{C}(\text{COOH})_2 \end{array}$

This acid has already been obtained by the hydrolysis of ethylic tetramethylenetetra-carboxylate by means of alcoholic potash, the crude product being purified by conversion into the lead salt (Trans., 1887, 51, 21), but, in preparing large quantities of this acid, this method proved too laborious, and after many experiments the following was adopted as being the most convenient and yielding the purest product.

In the first place, ethylic butanetetra-carboxylate was converted into ethylic tetramethylenetetra-carboxylate in the same way as before, with this slight difference, that in all cases a slight excess of sodium and of bromine were employed, so as to ensure the product being free from unchanged ethylic butanetetra-carboxylate, as even small quantities of the latter render the subsequent purification of the tetramethylene derivatives a matter of considerable difficulty. The quantities used in each operation were, 35 grams of ethylic butanetetra-carboxylate, 5 grams of sodium, and 18 grams of bromine; the crude ethereal salt was isolated as before, and at once converted into tetramethylenetetra-carboxylic acid.

For this purpose, the crude ethereal salt was digested on a water bath with  $1\frac{1}{2}$  times the calculated quantity of a strong, hot solution of pure barium hydroxide; hydrolysis took place very rapidly, the liquid becoming almost solid, owing to the separation of insoluble barium tetramethylenetetra-carboxylate. After heating for two hours, the mixture was vigorously boiled on a sand bath for half an hour, and the precipitated sandy barium salt collected by aid of the pump, and washed well with hot water. The barium salt was then stirred up with a quantity of boiling water and exactly decomposed by dilute sulphuric acid, great care being taken that no trace of sulphuric acid was left in the product, as otherwise charring would take place during the subsequent purification of the anhydride of tetramethylenedicarboxylic acid (p. 582) by distillation.

The filtrate from the barium sulphate was evaporated to a small bulk on a water bath and allowed to stand, when, after some days, beautiful colourless crystals of nearly pure tetramethylenetetra-carboxylic acid separated. These were collected by aid of the pump, drained on a porous tile, dissolved in a small quantity of water, and the solution allowed to concentrate over sulphuric acid in a vacuum.

The magnificent glistening crystals which formed were collected and exposed to the air for some days; they then contained two molecules of water of crystallisation.

	Found.		Theory.
	I.	II.	$C_8H_8O_8 + 2H_2O$ .
$H_2O$ .....	13.50	13.58	13.43

These crystals lose their water of crystallisation rapidly at  $100^\circ$ , and more slowly in a desiccator over sulphuric acid in a vacuum, becoming quite opaque. For analysis the substance was dried at  $100^\circ$ .

	Found.		Theory.
			$C_8H_8O_8$ .
C .....	41.38	per cent.	41.38
H .....	3.60	„	3.45

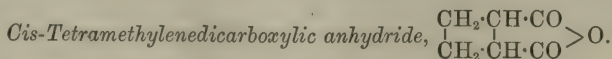
When heated rapidly in a capillary tube, tetramethylenetetracarboxylic acid decomposes at about  $198$ — $203^\circ$  with evolution of carbonic anhydride, and formation of tetramethylenedicarboxylic acid (or its anhydride), but small quantities of impurity and also the rapidity of heating very much influence the observed decomposing point; the temperature  $145$ — $150^\circ$ , previously given (*loc. cit.*, p. 22), is certainly much too low.

It dissolves very readily in water, alcohol, and ether, and behaves in all respects like a saturated acid. Its solution in sodium carbonate does not decolorise permanganate, even on long standing.

The *silver salt* of tetramethylenetetracarboxylic acid was obtained as a white, amorphous precipitate on adding silver nitrate to a faintly alkaline solution of the ammonium salt; it was collected, washed well with water, and dried over sulphuric acid in a vacuum. This salt decomposes very suddenly when heated, leaving a voluminous mass of spongy silver. For combustion it was intimately mixed with finely divided copper oxide, and the silver was determined in the wet way by Carius' method.

	Found.		Theory.
			$C_8H_4Ag_4O_8$ .
C .....	14.36	per cent.	14.54
H .....	0.82	„	0.60
Ag .....	65.40	„	65.45

The neutral solution of the ammonium salts shows the following behaviour with reagents:—*Lead acetate*, a white, amorphous precipitate; *barium nitrate*, a white, gelatinous precipitate; *calcium chloride*, no precipitate; *copper sulphate*, no immediate precipitate; but on standing the copper salt gradually separates as a light blue precipitate—



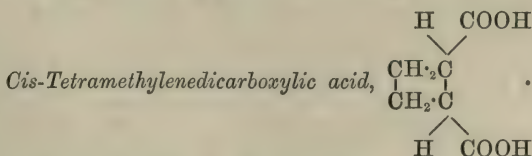
This may be readily obtained from the crude tetramethylenetetracarboxylic acid prepared as described above. For this purpose the

filtrate from the barium sulphate is evaporated to dryness, and the syrupy mass thus obtained is heated in an oil bath at  $200^{\circ}$  until the evolution of carbonic anhydride has ceased; the dark brown residue is then digested with three times its volume of acetyl chloride for two hours, the excess of acetyl chloride and acetic acid distilled off, and the crude tetramethylenedicarboxylic anhydride purified by fractionation under reduced pressure (160 mm.). If the product is free from adipic acid (arising from the decomposition of butanetetra-carboxylic acid present in the crude tetramethylenetetra-carboxylic acid, *loc. cit.*, p. 20) the whole distils, after twice fractioning, between  $210$ — $212^{\circ}$  as a colourless oil, which solidifies completely on cooling, and consists of pure tetramethylenedicarboxylic anhydride. This substance is difficult to burn, and requires a very hot tube, the combustion being conducted very slowly. The following results were obtained.

	Found.		Theory. $C_6H_6O_3$ .
	I.	II.	
C .....	57.15	57.10 per cent.	57.14 per cent.
H.....	5.03	4.89 „	4.76 „

It is difficult to decide what the correct melting point of this anhydride is. Using the products from different preparations, it was observed on several occasions, that when the melted substance is stirred with a thermometer as the mass gradually solidifies, the temperature remains constant at  $71^{\circ}$ . If, however, a strong solution of this anhydride in acetyl chloride is allowed to slowly evaporate over potash, beautiful, colourless crystals are deposited, which melt at about  $77^{\circ}$ , this then probably represents the correct melting point of the substance, and agrees closely with that previously found ( $76$ — $78^{\circ}$ ). When melted on a watch glass, the anhydride gives off vapours which are very irritating to the throat and produce violent coughing; it distils, under ordinary pressures, almost without decomposition, at about  $270$ — $273^{\circ}$ .

The pure anhydride dissolves only very slowly in cold water, but readily on warming, with formation of *cis*-tetramethylenedicarboxylic acid. It is readily soluble in alcohol and ether.



When tetramethylenedicarboxylic anhydride is dissolved in a little boiling water, and the solution allowed to concentrate over sulphuric



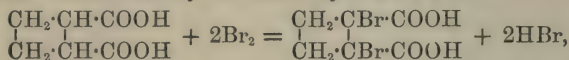
acid in a vacuum, *cis*-tetramethylenedicarboxylic acid gradually crystallises in magnificent transparent plates. These were freed as far as possible from the thick mother liquor by filtration on a pump, drained on a porous tile, and recrystallised from a small quantity of water, or from hydrochloric acid. For analysis, the substance was dried at 100°.

	Found.			Theory. $C_4H_6(COOH)_2$ .
	I.	II.		
C .....	49.91	50.05	per cent.	50.00 per cent.
H .....	5.62	5.70	,,	5.56 ,,

This acid melts at 137—138° and not at 130° as previously stated; it is very readily soluble in water, but much more sparingly in concentrated hydrochloric acid, from which it crystallises well. The dissociation constant for the electric conductivity of this acid was kindly determined by Dr. Walker, who obtained the result  $K = 0.0066$ ; this value is identical with that for succinic acid, and very much lower than that of the corresponding *cis*-pentamethylenedicarboxylic acid ( $K = 0.0158$ ).

Tetramethylenedicarboxylic acid has all the properties of a saturated acid; its solution in sodium carbonate does not decolorise permanganate, even on long standing, and, on boiling, action only takes place very slowly.

When treated with bromine and amorphous phosphorus it readily yields dibromotetramethylenedicarboxylic acid, thus—



a decomposition which is at the present time being carefully investigated.

*Methylic Salt of Cis-Tetramethylenedicarboxylic acid.*—In preparing large quantities of *cis*-tetramethylenedicarboxylic acid, the method usually employed was to heat the crude tetrabasic acid at 200° until carbonic anhydride ceased to be evolved, and then to dissolve the dark-brown residue in methyl alcohol and by the addition of sulphuric acid, or by saturating with hydrogen chloride, to convert the whole into the methylic salt. After two days, the product was poured into water, the oil which separated extracted with ether, the ethereal solution washed well with water and dilute sodium carbonate solution, dried over calcium chloride, and the ether distilled off. The residual oil on fractionation under reduced pressure (80—100 mm.) distilled fairly constantly at about 185°.

	Found.		Theory. $C_4H_6(COOCH_3)_2$ .
C .....	55.48	per cent.	55.81 per cent.
H .....	7.11	,,	6.98 ,,

Methylic *cis*-tetramethylenedicarboxylate is a colourless, pleasant smelling oil, which distils with very slight decomposition under ordinary pressures at about 225°; the corresponding ethylic salt has already been described (Trans., 1887, 51, 23), and boils at 238—242° (720 mm.).

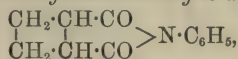
*Cis*-tetramethylenedicarboxylic acid is prepared from the methylic salt by digesting it with an excess of alcoholic potash for one hour; the product is dissolved in water, evaporated till free from alcohol, acidified, and the clear solution extracted three times with pure ether. The ethereal solution, after drying over calcium chloride, deposits the acid as a colourless oil, which solidifies completely on cooling, and may then be purified by recrystallisation from hydrochloric acid.

*Diamide of Tetramethylenedicarboxylic acid*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CONH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CONH}_2 \end{array}$ . This substance is very readily prepared by leaving the methylic salt of the acid in contact with concentrated aqueous ammonia: after standing for 24 hours, the aqueous layer is decanted from the crystalline cake which has formed, and the latter is purified by recrystallisation from water. The diamide separates from its hot, concentrated, aqueous solution, on cooling, in magnificent, colourless, transparent prisms, which are readily soluble in hot water and alcohol, but only sparingly in these solvents in the cold; it melts at about 228°, and when strongly heated, gives off ammonia, and a crystalline substance distils which is probably the corresponding imide.

Analysis.

	Found.	Theory. $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$
N.....	19.79 per cent.	19.70 per cent.

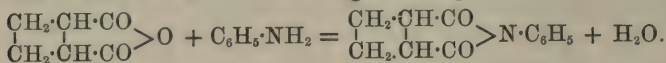
*Phenylimide of Tetramethylenedicarboxylic acid*,



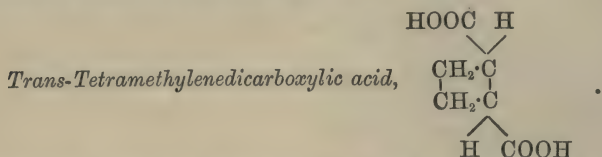
is readily prepared by heating a mixture of the anhydride of the acid with excess of pure aniline for about 10 minutes to boiling. The product is poured into a large volume of dilute hydrochloric acid, to remove excess of aniline, and the solid mass which separates is collected, washed with water, and recrystallised first from 50 per cent. alcohol, and then from methyl alcohol. The magnificent glistening needles thus obtained were dried at 100° and analysed with the following result.

	Found.		Theory. $\text{C}_{12}\text{H}_{11}\text{NO}_2$
	I.	II.	
C.....	71.74	—	71.64 per cent.
H.....	5.75	—	5.47 „
N.....	6.45	6.77	6.96 „

This substance is formed according to the equation



It melts at 127°, and crystallises so readily that it serves as a valuable means of identifying tetramethylenedicarboxylic acid. It is easily soluble in methyl and ethyl alcohol and in benzene, very sparingly in light petroleum and cold water; hot water, however, dissolves it more readily, and, on cooling, deposits it in magnificent glistening needles. It also crystallises well from a mixture of benzene and light petroleum, or from 50 per cent. alcohol. When heated in small quantities in a test-tube it distils without decomposition.



This interesting acid was obtained by heating *cis*-tetramethylenedicarboxylic acid with concentrated hydrochloric acid for 3—4 hours at 190°; the product, which contained crystals, and also some specks of carbon, was heated to boiling to dissolve the crystals, filtered, and the filtrate evaporated to a small bulk, and allowed to stand for 24 hours; the crystals, which had separated, were then collected and recrystallised 3 or 4 times from hydrochloric acid with the addition of animal charcoal. In this way, the pure *trans*-acid was obtained in beautiful, colourless needles, which, after drying at 100°, gave the following results on analysis.

	Found.	Theory.
C .....	49·82 per cent.	50·00 per cent.
H .....	5·57 „	5·56 „

*Trans*-tetramethylenedicarboxylic acid melts at 131°, or about 7° lower than the *cis*-modification, from which it differs in a marked manner in many important particulars.

The *cis*-acid is very readily converted into an anhydride. It is only necessary to boil it with acetyl chloride for five minutes to completely convert it into its anhydride, which is deposited in beautiful crystals, melting at about 75°, when the excess of acetyl chloride is allowed to evaporate over potash in a vacuum desiccator.

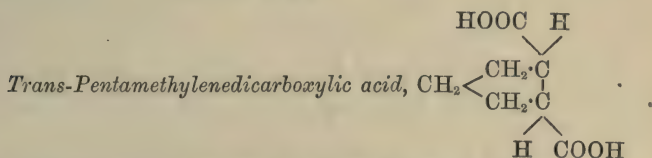
Under exactly similar conditions, the *trans*-acid remains quite unacted on, and, even when heated at 160° with excess of acetyl chloride, in a sealed tube for one hour, no anhydride appears to be formed, as was shown by the fact that the crystals which separated as the acetyl chloride evaporated melted at 127—129°, and were very

readily soluble in water. An analysis showed that these crystals consisted of unchanged acid.

	Found.	Theory. $C_4H_6(COOH)_2$ .
C .....	49.61 per cent.	50.00 per cent.
H .....	5.72 „	5.56 „

When, however, *trans*-tetramethylenedicarboxylic acid is repeatedly distilled under ordinary pressures, elimination of water does gradually take place, and, after four distillations, the product has the appearance of the anhydride of the *cis*-acid; it melts for the most part at  $70^\circ$ , but a small quantity is always left which does not melt until a higher temperature; this experiment therefore seems to show that *trans*-tetramethylenedicarboxylic acid on distillation is converted partially into the anhydride of the *cis*-acid.

Dr. Walker also found that the *cis*- and *trans*-acids had very different dissociation constants, for the *cis*-acid (m. p.  $138^\circ$ )  $K = 0.0066$ , whereas in the case of the *trans*-acid (m. p.  $130$ – $131^\circ$ ) the constant found was  $K = 0.0028$ .



In investigating this acid, it was found that the method of preparing it previously adopted (Trans., 1887, **51**, 244) was not altogether satisfactory, the purification of the crude product by conversion into the ethylic salt as there described being attended with unnecessary loss of time and material.

After many experiments, the best yield of acid was obtained by modifying the process in the following way. The crude ethylic pentamethylenetetracarboxylate, obtained by the action of bromine on the disodium compound of ethylic pentanetetracarboxylate, was dissolved in glacial acetic acid (2–3 vols.), concentrated sulphuric acid (1 vol.) and water (1 vol.) added, and the whole heated in a reflux apparatus for about two days, until hydrolysis was complete, as shown by the fact that a drop of the liquid dissolved in much water form a clear solution.

A rapid current of steam was then passed into the boiling, brownish liquid until the odour of acetic acid was no longer apparent, and the product allowed to remain for two days in a cool place. At the end of this time, the brownish, crystalline crust which had separated was collected, washed with a little water, and purified by crystallisation from water with the aid of animal charcoal. Pure

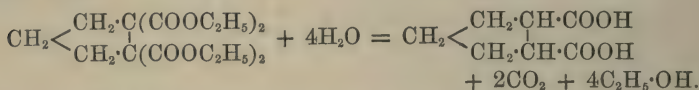


*trans*-pentamethylenedicarboxylic acid was thus readily obtained as a colourless, sandy, crystalline powder, which, after drying at 100°, melted at 160° and gave the following results on analysis.

	Found.	Theory. C <sub>5</sub> H <sub>8</sub> (COOH) <sub>2</sub> .
C .....	53.10 per cent.	53.16 per cent.
H .....	6.37 „	6.33 „

The dark-coloured mother liquors separated from the crystalline acid, if extracted with ether, yield a further quantity of crude acid, which is, however, somewhat difficult to purify, and is best employed in the preparation of the anhydride of the *cis*-acid (see below).

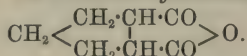
The hydrolysis of ethylic pentamethylenetetra-carboxylate by the above method is attended with the loss of 2 mols. of carbonic anhydride, and the direct formation of *trans*-pentamethylenedicarboxylic acid.



The yield of acid obtained in this way is certainly better than that previously obtained, and, as the operation takes less time, it was adopted in preparing the acid required for this research.

The properties of *trans*-pentamethylenedicarboxylic acid have already been given (Trans., 1887, 51, 246); in addition, it should be mentioned that the solution of the acid in sodium carbonate does not decolorise permanganate in the cold, and only very slowly on boiling the behaviour of the acid when treated with bromine and phosphorus is being investigated.

*Anhydride of Cis-Pentamethylenedicarboxylic acid,*



In view of Baeyer's suggestion (*Annalen*, 257, 179), that *trans*-pentamethylenedicarboxylic acid should yield an anhydride isomeric with, and readily convertible into, the anhydride of the *cis*-acid, very careful experiments on the action of acetyl chloride on this acid were made with the following results.

The acid was somewhat sparingly soluble in cold acetyl chloride, but dissolved readily on warming; the solution was heated to boiling in a reflux apparatus for half an hour, but no formation of anhydride took place, and on distilling off the bulk of the acetyl chloride and allowing the solution to stand over potash under reduced pressure,

the unchanged acid crystallised out in nodular masses melting at 155—158°.

A second experiment, in which the solution of the acid in acetyl chloride was heated at 100° in a sealed tube for one hour, gave a similar result, as is shown by an analysis of the crystals melting at 154—156°, which were obtained by allowing the product to evaporate over potash in a desiccator.

	Found.	Theory. $C_5H_8(COOH)_2$ .
C .....	52·51 per cent.	53·16 per cent.
H .....	6·45     „	6·33     „

In the next experiment, the acid was heated in a sealed tube with a large excess of acetyl chloride at 140° for about one hour. On opening the tube, considerable pressure was observed, and the almost colourless liquid, on evaporation, deposited a thick oil; this on standing over potash for a few days, deposited a quantity of colourless crystals which were collected by the aid of the pump, and freed from adhering mother liquor by placing them on a porous tile. They melted at 70—72°, and consisted of the anhydride of the *cis*-acid (see below).

In order to be sure that the isomeric anhydride of the *trans*-acid was not contained in the mother liquors from these crystals, the thick, somewhat dark-coloured, filtrate, was dissolved in warm dilute potash, the solution filtered, acidified, and allowed to stand in a cool place. The beautiful colourless crystals which separated melted at 140—141°, and consisted of pure *cis*-pentamethylenedicarboxylic acid, no trace of the *trans*-acid being present. It appears certain, therefore, that no anhydride of the *trans*-acid is formed under the conditions observed in the above experiments.

The best method of preparing the anhydride of *cis*-pentamethylenedicarboxylic acid in quantity is to digest the crude *trans*-acid, obtained as explained on p. 587, with acetic anhydride for two hours, and then to fraction the product under reduced pressure (160 mm.). After two distillations, the whole passes over at about 220° as an almost colourless oil, which, on cooling, sets to a semi-solid gelatinous mass; this, after a time, gradually becomes crystalline. Although this substance distils at a constant temperature, it is not quite pure, but contains, apparently, small quantities of unchanged acid, as the following analysis shows.

	Found.	Theory.	
		$C_5H_8C_2O_3$ .	$C_5H_8(COOH)_2$ .
C .....	58·91 per cent.	60·00	53·16 per cent.
H .....	6·22     „	5·71	6·33     „

If, however, it is dissolved in twice its volume of acetic anhydride,

and the solvent allowed to evaporate gradually over potash under reduced pressure, the pure anhydride separates in magnificent, hard, colourless, tabular prisms; these were collected, washed with a little acetic anhydride, and analysed.

	Found.		Theory. $C_5H_8C_2O_3$ .
	I.	II.	
C .....	59.95	59.96 per cent.	60.00 per cent.
H .....	5.98	6.12 „	5.71 „

The anhydride of *cis*-pentamethylenedicarboxylic acid melts at about 73° to a colourless oil, which, on cooling, sets to a semi-transparent gelatinous mass of about the consistency of paraffin wax. When rubbed with a glass rod, or touched with a crystal of the anhydride, it gradually crystallises in a very characteristic manner, and it is interesting to note that the anhydride of *cis*-hexahydrophthalic acid behaves in a similar way when melted and allowed to solidify (Baeyer, *Annalen*, 258, 219).

The anhydride of *cis*-pentamethylenedicarboxylic acid is insoluble in and only very slowly attacked by cold water, but it dissolves readily on boiling, and on cooling, if the solution be sufficiently concentrated, the *cis*-acid separates in beautiful, glistening needles. The anhydride is readily soluble in ether, alcohol, or benzene, but only sparingly in light petroleum.

In the previous paper on pentamethylenedicarboxylic acid (Trans., 1887, 51, 248), it was mentioned that this acid, if heated at 300° and subsequently distilled, yielded an anhydride melting at 64—67°. This observation is correct, but the substance, after recrystallisation from acetic anhydride, melts at 72—73°.

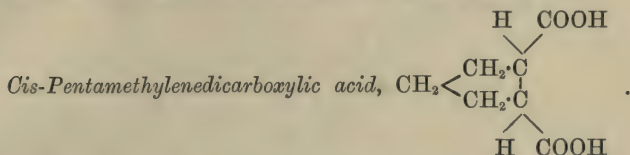
*Phenylimide of Pentamethylenedicarboxylic acid*,  $C_6H_5 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > N \cdot C_6H_5$ .

In order to prepare this substance, the anhydride of *cis*-pentamethylenedicarboxylic acid was heated to boiling with excess of aniline for about 15 minutes, the product poured into water, excess of dilute hydrochloric acid added, and the whole well stirred until the oily drops had completely solidified. The brownish product was readily purified by recrystallisation once from dilute methyl alcohol, and twice from a mixture of benzene and light petroleum.

N .....	Found.	Theory. $C_{13}H_{13}NO_2$ .
	6.90 per cent.	6.51 per cent.

This phenylimide is sparingly soluble in cold water, more readily in hot, crystallising from the solution as it cools in magnificent, glistening needles, which melt at 89°. It dissolves readily in alcohol,

benzene, and acetic acid, but is only sparingly soluble in light petroleum. When rapidly heated in small quantities, it distils without decomposition, the distillate solidifying to hard, transparent balls, which remain in this condition sometimes for days, but crystallise at once when touched with a crystal of the substance.



In order to prepare this acid, the anhydride just described was dissolved in dilute potash, and the concentrated solution acidified and allowed to stand; the long, needle-shaped crystals which separated were then collected, and recrystallised twice from water.

The analysis of the pure substance, dried at 100°, gave the following results.

	Found.		Theory.
	I.	II.	$\text{C}_5\text{H}_8(\text{COOH})_2$ .
C .....	53.04	53.10 per cent.	53.16 per cent.
H .....	6.42	6.40 „	6.33 „

*Cis*-pentamethylenedicarboxylic acid melts at 140°, and is, at this temperature, gradually converted into its anhydride with loss of water, the change taking place very rapidly at 150—160°.

It is much more readily soluble in water than the *trans*-modification, and crystallises from the hot concentrated solution in beautiful, colourless needles, whereas the *trans*-acid is deposited in the form of a sandy, crystalline powder, the difference in appearance being, in fact, very much the same as in the case of maleïc and fumaric acids.

The *cis*-acid is readily soluble in acetyl chloride, and, on heating the solution at 100°, it seems to be quantitatively converted into its anhydride, which crystallises in plates when the product is allowed to evaporate over potash in a vacuum.

The *cis*-acid may be readily converted into the *trans*-acid by heating it with hydrochloric acid at 180° for two hours; the sealed tube in which the experiment was conducted was found to be filled with hard crystals, somewhat discoloured by specks of charcoal. The contents of the tube were warmed with water until the crystals had completely dissolved, and the solution filtered; on standing, the pure *trans*-acid was deposited as a sandy powder, which, after recrystallisation, melted at 160°, and, on analysis, gave the following results.

	Found.	Theory.
		$\text{C}_5\text{H}_8(\text{COOH})_2$ .
C .....	53.21 per cent.	53.16 per cent.
H .....	6.36 „	6.33 „



As far as could be judged from a small experiment, the conversion of the *cis*- into the *trans*-modification by heating with hydrochloric acid was complete.

*Chemical Laboratory,*  
*Owens College,*  
*Manchester.*

# 1 : 2-PENTAMETHYLENEDICARBOXYLIC ACID.

BY

E. HAWORTH, B.Sc.,

AND

W. H. PERKIN, JUN.

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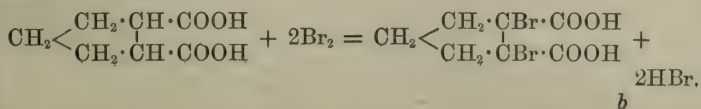
[From the Transactions of the Chemical Society, 1894.]



### 1 : 2-Pentamethylenedicarboxylic acid.

By E. HAWORTH, B.Sc., and W. H. PERKIN, jun.

THE anhydride of *cis*-pentamethylenedicarboxylic acid behaves towards bromine, in the presence of phosphorus, in a manner similar to the anhydride of *cis*-tetramethylenedicarboxylic acid (see preceding paper), the principal product of the action being *dibromopentamethylenedicarboxylic acid*,

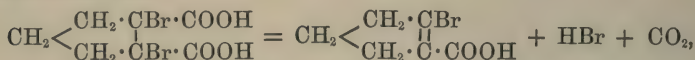




but the yield of this acid is comparatively small, as much carbonaceous matter is produced during the bromination and during the subsequent purification of the substance by recrystallisation from hydrobromic acid.

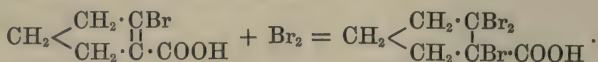
This tendency to decompose into carbon and hydrogen bromide, when heated with bromine, has been previously observed in the case of pentamethylenedicarboxylic acid (Trans., 1887, **51**, 247), and may possibly be characteristic of pentamethylene derivatives; in the experiment referred to here, the pure bibasic acid was heated with bromine water at 180° for four hours, at the end of which time it had completely decomposed into carbon and hydrogen bromide.

*Dibromopentamethylenedicarboxylic acid* is a colourless, crystalline substance, which melts at 183–184°; it cannot be distilled, and all attempts to obtain an anhydride with the aid of acetyl chloride, &c., failed, owing to the instability of the acid; when treated with alkalis, it is readily decomposed with formation of *bromodihydropentenecarboxylic acid*, thus—

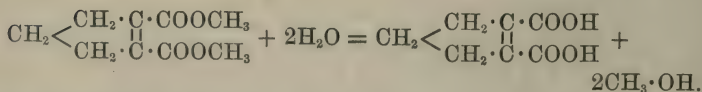
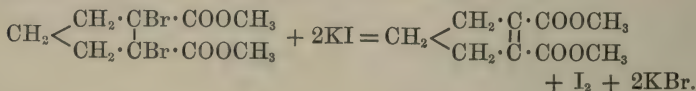


just as under similar conditions dibromotetramethylenedicarboxylic acid yields bromodihydotetrenecarboxylic acid.

This new acid crystallises from water in needles, melts at about 130°, and, in contact with bromine vapour, is rapidly converted into *tribromopentamethylenecarboxylic acid*,



*Dihydropentenedicarboxylic acid* is produced when methylic dibromopentamethylenedicarboxylate is digested with potassium iodide in alcoholic solution, and the product hydrolysed with potash.

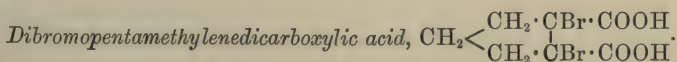


It crystallises in colourless prisms, melts at 178°, and is much less readily converted into an anhydride than the corresponding dihydro-tetrenedicarboxylic acid, from which it also differs in that it is converted by contact with bromine vapour into dibromopentamethylenedicarboxylic acid, whereas under these circumstances the tetrene acid remains unchanged.

Experiments are also described in this paper, made with the object of preparing the anhydride of *trans*-pentamethylenedicarboxylic acid; as this anhydride should, according to Baeyer's views (*Annalen*, **257**, 179), be capable of existence, and should, indeed, be as readily produced as the anhydride of *trans*-hexahydrophthalic acid. As, however, *trans*-pentamethylenedicarboxylic acid is not appreciably acted on by acetyl chloride at 100° (this vol., 587), and at 140° yields the anhydride of the *cis*-acid, results which Baeyer was kind enough to confirm, it seemed unlikely that the *trans*-anhydride could be isolated even if it existed.

However, at Baeyer's suggestion, we systematically studied the action of acetic anhydride on the pure *trans*-acid, and as the result of a large number of experiments we find that the almost pure *trans*-anhydride is formed when the acid is digested with acetic anhydride for 25 minutes and the excess of acetic anhydride removed by passing a current of dry air through the product heated at 120° under 20 mm. pressure; it is an oil which contains traces of the anhydride of the *cis*-acid, into which it is completely converted by distillation.

The analogy between the dimethylsuccinic acids, the hexahydrophthalic acids, and the pentamethylenedicarboxylic acids is now complete, the only remarkable point being that whereas the anhydrides of the *trans*-modifications of the two first-named acids are so easily formed, *trans*-pentamethylenedicarboxylic acid can only be converted into its anhydride with considerable difficulty.



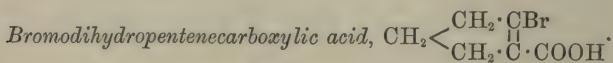
In order to prepare this substance, *cis*-pentamethylenedicarboxylic anhydride (10 grams) was mixed with amorphous phosphorus (2 grams), dry bromine (60 grams) gradually added, with constant cooling, and the whole heated in a reflux apparatus for six hours to boiling; torrents of hydrogen bromide were given off, and the action appeared to proceed in much the same way as in the case of the formation of dibromotetramethylenedicarboxylic acid (p. 966). A further quantity of bromine (30 grams) and amorphous phosphorus (1 gram) was then added, and the heating continued for six hours longer; the product, after being freed from excess of bromine by blowing in air, was poured into a large quantity of water, care being taken to keep the temperature below 30° by cooling with water. After about an hour, the heavy oil was extracted with ether, the ethereal solution filtered from a considerable quantity of carbonaceous matter, washed with a little dilute sodium hydrogen sulphite solution to remove the last traces of bromine, dried by calcium chloride,

evaporated, and the dark-coloured, oily residue allowed to stand over sulphuric acid in a vacuum for about a week. At the end of that time, the thick, prismatic crystals which had separated were freed as far as possible from the dark, oily, mother liquor by decantation, allowed to remain in contact with porous porcelain until quite colourless, ground up, and recrystallised twice from fuming hydrobromic acid.

In this way, colourless, glistening crystals were obtained, which, after drying at 100°, gave the following results on analysis.

	Found.			Theory.
	I.	II.		$C_6H_6Br_2(COOH)_2$ .
C .....	26.71	27.24	per cent.	26.58 per cent.
H .....	2.84	2.95	,,	2.53 ,,
Br .....	50.21	49.69	,,	50.63 ,,

Dibromopentamethylenedicarboxylic acid melts at 183—184° with evolution of gas; it is readily soluble in warm water, alcohol, and ether, and in hot concentrated hydrochloric or hydrobromic acids, but only sparingly in the cold acids. In general properties, it resembles the corresponding dibromotetramethylenedicarboxylic acid, except that it is less stable and very readily carbonises when treated with reagents or when heated; thus, for example, all attempts to prepare its anhydride by distillation under diminished pressure failed, owing to the acid decomposing into a carbonaceous mass with evolution of hydrogen bromide in abundance. When heated with acetic anhydride in a reflux apparatus, the solution rapidly darkened and ultimately became almost black, hydrogen bromide being evolved; on distilling the product under reduced pressure (20 mm.) decomposition set in as soon as the acetic anhydride had passed over; many other experiments were made with the object of preparing the anhydride, but in no case could a crystalline compound be isolated.



This is formed when alcoholic potash acts on dibromopentamethylenedicarboxylic acid. The pure dibromo-acid (5 grams) was added in small quantities at a time to a strong boiling solution of pure potash (10 grams) in ethylic alcohol; a vigorous action set in, potassium bromide separated, and at the same time the mass became dark coloured. After boiling for a few minutes, using a reflux condenser, water was added, the dark brown solution, filtered from small quantities of carbonaceous matter, was acidified, and extracted five times with ether; the ethereal solution, after being washed well with

water, and dried over calcium chloride, was evaporated, and the crystalline residue left in contact with porous porcelain for some hours until free from oily mother liquor. The crude residual substance was then purified by repeated recrystallisation from water with the aid of animal charcoal, and the colourless crystals analysed.

	Found.			Theory.
	I.	II.		$C_5H_6Br \cdot COOH$ .
C .....	38.15	38.02	per cent.	37.69 per cent.
H .....	4.08	3.94	,,	3.66 ,,
Br .....	42.13	42.01	,,	41.88 ,,

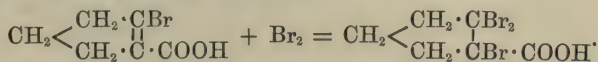
Bromodihydropentenecarboxylic acid melts at about  $130^\circ$ , but softens a few degrees lower, and, when strongly heated, distils without leaving any residue and apparently without undergoing decomposition; it is readily soluble in alcohol, ether, benzene, chloroform, formic acid, and hot water or light petroleum, but only sparingly in the two latter solvents in the cold; it crystallises best from hot water.

The solution of the acid in dilute sodium carbonate decolorises permanganate rapidly.

Bromodihydropentenecarboxylic acid is apparently not the only product of the action of alcoholic potash on dibromopentamethylenedicarboxylic acid, but the other substance or substances present in the mother liquor of this acid could not be isolated in quantity sufficient for analysis.



This acid is formed quantitatively when bromodihydropentenecarboxylic acid is exposed to the action of bromine vapour.



0.5546 gram of pure bromodihydropentenecarboxylic acid left in contact with *dry* bromine vapour for 24 hours, and then freed from excess of bromine by exposure over potash in a vacuum, had gained 0.481 gram in weight, whereas, in the formation of the tribromo-acid, according to the above equation, theoretically 0.464 gram of bromine should have been taken up. The product is highly unstable, but, with care, it may be recrystallised from formic acid, and is thus obtained in colourless nodular masses, about half of the substance remaining in the mother liquor.

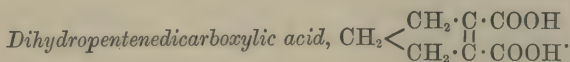
The pure substance, on analysis, gave the following result.



	Found.	Theory. $C_6H_7Br_3O_2$ .
Br.....	68.04 per cent.	68.37 per cent.

Tribromopentamethylenecarboxylic acid is readily soluble in ether and alcohol, but only sparingly in water, formic acid, or light petroleum; it is very readily decomposed when boiled with water, hydrogen bromide being eliminated.

The freshly-prepared solution of the acid in cold sodium carbonate does not decolorise permanganate instantaneously, but oxidation takes place slowly on standing, and very rapidly if the solution is warmed, due doubtless to the gradual decomposition of the tribromo-acid into unsaturated compounds.



In order to prepare this beautiful crystalline substance, the following method was employed.

The crude product of the action of bromine and phosphorus on pentamethylenedicarboxylic acid, after removal of excess of bromine by blowing in air (p. 980), was treated with methylic alcohol; and as soon as the mixture had cooled down it was poured into water, and the crude methylic salt which separated as a dark-coloured heavy oil extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution, dried over anhydrous potassium carbonate, filtered, and evaporated. The dark-coloured, oily residue, consisting of crude methylic dibromopentamethylenedicarboxylate, did not deposit crystals, even after standing for some days over sulphuric acid in a vacuum, and therefore no analysis was made.

This crude methylic salt was dissolved in alcohol, a large excess of powdered potassium iodide added, and the whole heated in a reflux apparatus for two hours; iodine was liberated in abundance, and the action appeared to proceed exactly as in the case of the decomposition of methylic dibromotetramethylenedicarboxylate under similar conditions (p. 974). To the product, mixed with water, sufficient dilute sodium hydrogen sulphite solution was added to remove the free iodine, and the oily methylic salt extracted twice with ether; the ethereal solution was then dried over calcium chloride, evaporated, and the residual, oily, ethereal salt at once converted into the corresponding acid by hydrolysis with potash. After boiling with excess of alcoholic potash for about five minutes, the solution was diluted with water, evaporated on a water bath till free from alcohol, acidified, and extracted 15 times with ether; the dark, crystalline mass which remained after distilling off the ether was purified by recrystallisation,

first from water with the aid of animal charcoal, and then from ether. Analysis,

	Found.		Theory.
	I.	II.	$C_5H_6(COOH)_2$ .
C .....	53.90	53.77 per cent.	53.84 per cent.
H .....	5.46	5.33 „	5.13 „

Dihydropentenedicarboxylic acid crystallises in hard, glistening, transparent crystals, and melts unaltered at about  $178^\circ$ ; it is readily soluble in hot water, alcohol, acetic acid, and acetic anhydride, moderately in ether, but only sparingly in benzene, light petroleum, and cold water. It is a strong acid; its aqueous solution is strongly acid to litmus, and even thick crystals effervesce vigorously when brought in contact with sodium carbonate solution; a dilute solution of its sodium salt decolorises permanganate, although not so instantaneously as the sodium salts of many other unsaturated acids. In its behaviour towards bromine vapour, this acid appears to differ in a very marked manner from the corresponding dihydrotetrenedicarboxylic acid; a small quantity of the former was exposed to dry bromine vapour under a bell-jar during two days, the reddish-coloured product was freed from bromine over potash in a vacuum dessicator, and the residue recrystallised from hydrobromic acid. The crystals obtained melted and decomposed at  $180^\circ$ , and as they contained bromine, they probably consisted of dibromopentamethylenedicarboxylic acid; unfortunately the identity could not be proved by analysis, owing to the small quantity of material at our disposal; under similar conditions, dihydrotetrenedicarboxylic acid remains unchanged.

In its behaviour when heated, dihydropentenedicarboxylic acid differs also in a marked manner from the corresponding tetrene derivative; the latter, on distillation, carbonises and is entirely decomposed, whereas the former, if rapidly heated, distils without decomposition, the solid distillate melting at  $175$ — $177^\circ$ . If, however, the pentene acid be heated for 10 minutes in a narrow test-tube in such a way that the distillate constantly runs back, and the product be then distilled, an oily distillate will be obtained which, on long standing, becomes opaque from separation of a small quantity of a crystalline substance, and, on warming with water, it first melts and then gradually passes into solution. On standing over sulphuric acid in a vacuum, the aqueous solution deposits a small quantity of dihydropentenedicarboxylic acid, and the filtrate from these crystals, on evaporation, dries up to a gummy residue, which resembles the product obtained on dissolving the anhydride of dihydrotetrenedicarboxylic acid in water; it could not be analysed, the quantity being insufficient.

*Salts of Dihydropentenedicarboxylic acid.*

*Hydrogen Silver Salt*,  $\text{COOH} \cdot \text{C}_5\text{H}_6 \cdot \text{COOAg}$ .—One of the most characteristic properties of dihydrotetrenedicarboxylic acid is the tendency which it shows to form a hydrogen silver salt, and this property is even more pronounced in the case of dihydropentenedicarboxylic acid.

The pure acid was dissolved in water, the solution rendered slightly alkaline with ammonia, warmed to about  $40^\circ$ , and excess of silver nitrate added, when a white precipitate separated, which was collected, washed with water, and dried over sulphuric acid in a vacuum.

When heated in a crucible, this salt decomposes suddenly with formation of voluminous threads of silver, and the amount of silver contained in the salt was found to be only 44.3 per cent., whereas the neutral salt,  $\text{C}_7\text{H}_6\text{O}_4\text{Ag}_2$ , would contain 58.38 per cent.; indeed, this analysis agrees very much better with the composition of the hydrogen silver salt,  $\text{C}_7\text{H}_7\text{O}_4\text{Ag}$ , which contains 41.08 per cent. of silver.

The mother liquors from this salt, on standing, deposited long, colourless needles which in appearance closely resemble the crystals of the hydrogen silver salt of dihydrotetrenedicarboxylic acid. They were collected, washed with water, and analysed with the following result.

	Found.	Theory. $\text{C}_7\text{H}_7\text{O}_4\text{Ag}$ .
Ag .....	41.41 per cent.	41.08 per cent.

This salt is, therefore, evidently the hydrogen silver salt.

A neutral solution of the ammonium salt of dihydropentenedicarboxylic acid shows the following behaviour with reagents.

*Lead acetate*; a white, gelatinous precipitate.

*Copper sulphate* and *barium nitrate*; no precipitate.

*Calcium chloride*; no precipitate at first, but, on standing, the calcium salt separates slowly in magnificent four-sided, glistening, tabular crystals.

*Anhydride of Trans-pentamethylenedicarboxylic acid.*

As explained in the introduction to this paper, considerable interest attaches to the preparation of an anhydride of *trans*-pentamethylenedicarboxylic acid, and many experiments were made with the object of obtaining this substance, of which only one or two can be described here.

The *trans*-acid used in these experiments was very carefully purified by repeated recrystallisation; it was then heated in sealed tubes

at 200° with concentrated hydrochloric acid, in order to free it from traces of the *cis*-acid which might possibly be present (compare this vol., 590), and then quantities of about 1 gram were heated with pure acetic anhydride to boiling on a reflux apparatus for 5, 10, 15, 20, and 25 minutes respectively. After standing for several days over potash in a vacuum, and until free from acetic anhydride, a very thick, oily residue was, in all cases, obtained, which, even when the heating had been continued for 25 minutes, gradually deposited varying quantities of unchanged acid, and all the samples, on standing, exposed to the air completely solidified to a cake of the pure acid in a few days.

Ultimately, a substance consisting evidently of nearly pure *trans*-pentamethylenedicarboxylic anhydride was obtained as follows.

The pure acid was heated with 10 times its weight of pure acetic anhydride on a reflux apparatus for 25 minutes, so that the liquid just boiled; the product was then transferred to a small Würtz flask, heated at 120° under a pressure of 20 mm., and a slow stream of carefully dried air allowed to pass through the liquid until the excess of acetic anhydride had been completely removed.

The slightly brownish residue gave, on analysis, the following numbers, which agree with those required for the anhydride of *trans*-pentamethylenedicarboxylic acid.

	Found.		Theory.
	I.	II.	$C_5H_8C_2O_3$ .
C .....	59.73	59.81 per cent.	60.00 per cent.
H .....	5.90	5.87     ,,	5.71     ,,

This substance is, however, not quite pure, and contains traces of the *cis*-anhydride, as was shown by the fact that when it was dissolved in hot water, and the solution allowed to cool, crystals were obtained which did not melt quite sharply at 160° (the m. p. of the *trans*-acid), and the mother liquor was found to contain traces of the *cis*-acid; nevertheless, there can be no doubt that the greater portion of the substance must have consisted of the anhydride of the *trans*-acid.

In its properties, this anhydride differs in many ways from the beautifully crystalline anhydride of the *cis*-acid; it dissolves, for example, in sodium carbonate very rapidly with effervescence, and when exposed to the air on a watch-glass, it gradually solidifies to a solid cake consisting principally of the *trans*-acid; the *cis*-anhydride, on the other hand, is stable in the air, and dissolves only very slowly in sodium carbonate.

Possibly this tendency to combine with water may account for the gradual deposition of *trans*-acid from the products of the time ex-



periments described above, as it is difficult to be certain that potash is dry, and, moreover, water would be produced by the absorption of the acetic acid.

The remainder of the *trans*-anhydride was distilled under reduced pressure, when a colourless distillate was obtained, which solidified in the manner so highly characteristic of the *cis*-anhydride; the distillate was dissolved in acetic anhydride and allowed to slowly evaporate over potash in a vacuum, when crystals gradually separated which melted at 70—71° (the *cis*-anhydride melts at 73°), and gave on analysis the following result.

	Found.	Theory. $C_5H_8C_2O_3$ .
C .....	59·68 per cent.	60·00 per cent.
H .....	5·89 „	5·71 „

It is, therefore, obvious that *trans*-pentamethylenedicarboxylic anhydride, on distillation, is converted into the anhydride of the *cis*-acid.

*Chemical Laboratory,  
Owens College, Manchester.*

SYNTHESIS OF PENTAMETHYLENECARBOXYLIC  
ACID, HEXAMETHYLENECARBOXYLIC ACID  
(HEXHYDROBENZOIC ACID), AND AZELAÏC  
ACID.

BY

E. HAWORTH, B.Sc.,

AND

W. H. PERKIN, JUN., PH.D., F.R.S.

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[From the Transactions of the Chemical Society, 1894.]



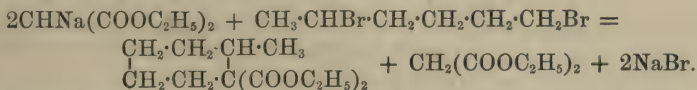
# Synthesis of pentamethylenecarboxylic acid, hexamethylenecarboxylic acid (hexahydrobenzoic acid), and azelaic acid

By E. HAWORTH, B.Sc., and W. H. PERKIN, Jun., Ph.D., F.R.S.

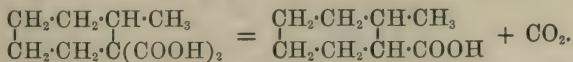
DURING the last few years, the behaviour of benzene derivatives on reduction has been the subject of much investigation, and Baeyer's classical researches in this field (*Annalen*, **245**, 103; **251**, 257; **269**, 145) have shown that, when subjected to the action of sodium amalgam, the phthalic acids yield a variety of interesting derivatives, the end product being in all cases the saturated hexahydro-acids formed by the complete reduction of the benzene ring. Although these acids contain a closed chain of six carbon atoms, they have none of the properties characteristic of benzene derivatives, but behave in almost all respects like saturated open chain acids of the fatty series.

Other hexahydrobenzene derivatives have also been obtained by the reduction of the corresponding benzene derivatives; but only in a very few instances have such compounds been synthetically prepared from substances belonging to the fatty series. One case of this kind, which has a special bearing on the present investigation, is the synthesis of 1:2-methylhexamethylenecarboxylic acid (hexahydro- $\alpha$ -toluic acid; Freer and Perkin, *Trans.*, 1888, **53**, 202), which was carried out in the following manner.

The sodium derivative of ethylic malonate was digested in alcoholic solution with methylpentamethylene dibromide, when reaction readily took place in accordance with the equation



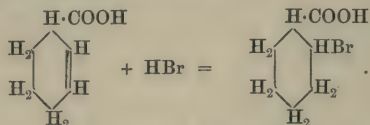
The ethylic methylhexamethylenedicarboxylate was converted by hydrolysis into the corresponding bibasic acid, which, when heated at  $200^\circ$ , was decomposed quantitatively into carbon dioxide and methylhexamethylenecarboxylic acid.



The action of reducing agents on  $\alpha$ -toluic acid has not as yet been investigated; and, therefore, it has not been possible to compare the reduced benzene derivative with the synthetical acid; some time since, however, Aschan (*Annalen*, **271**, 231) succeeded in converting

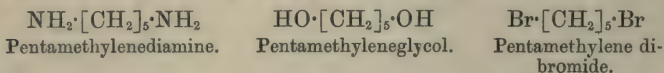


benzoic acid into hexahydrobenzoic acid, the method used being the following. In the first place, benzoic acid was reduced by excess of sodium amalgam in alkaline solution to  $\Delta^2$ -tetrahydrobenzoic acid; and, by treating this acid with hydrobromic acid, it was converted into  $\beta$ -(?) -bromhexahydrobenzoic acid.



Bromhexahydrobenzoic acid is readily reduced by sodium amalgam, yielding hexahydrobenzoic acid (hexamethylenecarboxylic acid). This important acid is very similar in its properties to the methylhexamethylenecarboxylic acid prepared synthetically by the method described above; and it appeared to us that it would be especially interesting to endeavour to obtain hexahydrobenzoic acid synthetically, as it would then be possible to compare the synthetical acid with the reduced benzene derivative.

For this purpose, pentamethylene dibromide,  $\text{Br}[\text{CH}_2]_5\text{Br}$ , was required, a substance which Gustavson and Demjanoff (*J. pr. Chem.*, **39**, 542) had already prepared from pentamethylenediamine by converting it into the corresponding glycol by the action of silver nitrite, and subsequently treating the glycol with hydrobromic acid.



Before commencing the study of the action of this dibromide on the sodium derivative of ethylic malonate, we wrote to Professor Gustavson, and in reply he informed us that Herr Demjanoff had already instituted experiments in this direction, but did not intend to proceed any further with them, and subsequently Herr Demjanoff not only agreed to allow us to continue this research, but he also very kindly gave us a detailed account of the results which he had obtained in his preliminary experiments.

The yield of pentamethylene dibromide obtained by Gustavson and Demjanoff (*J. pr. Chem.*, **39**, 542) was very small, only about 8 per cent. of the theoretical, and as we required considerable quantities of it, we, in the first place, made numerous experiments with the object of improving the method of preparation, but without success, so that ultimately we prepared our material by a method practically identical with that devised by Gustavson and Demjanoff. The preparation of the dibromide is exceedingly tedious: altogether 1500 grams of trimethylene bromide were used, the conversion of which into pentamethylene dibromide necessitated more than three months' steady

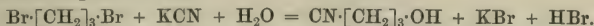
work, the ultimate amount of product obtained being only 90 grams.

The subsequent study of the action of this dibromide on the sodium compound of ethylic malonate yielded very remarkable results, which prove, as we believe, that the substance which was supposed to be comparatively pure pentamethylene dibromide is in reality a mixture of this substance and tetramethylene dibromide,  $\text{Br} \cdot [\text{CH}_2]_4 \cdot \text{Br}$ , the latter constituting, as it appears, as much as 70—75 per cent. of the whole. It is certainly very difficult to understand how tetramethylene dibromide can be thus produced from pentamethylenediamine; and it will hardly be possible to understand this remarkable method of formation, until a very careful examination of the action of silver nitrite on the hydrochloride of the diamine has been instituted, as the decomposition seems to be very complicated.\*

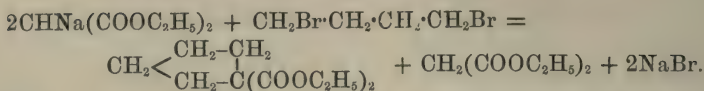
The reasons for assuming that the dibromide obtained by Gustavson and Demjanoff's method is a mixture, will be readily understood from the accompanying short sketch of the results obtained in investigating its action on the sodium derivative of ethylic malonate. In alcoholic solution, action takes place very readily on warming, with separation of sodium bromide and formation of an oily, ethereal salt, which, on distillation, yields, besides regenerated ethylic malonate, two principal fractions, 240—250° (760 mm.) and 270—275° (50 mm.). The fraction 240—250° contains traces of bromine, and, therefore, did not give good results on analysis; when hydrolysed by boiling with alcoholic potash, however, it yields a beautifully crystalline bibasic acid, which, on analysis, gave numbers agreeing sharply with those required by the formula  $\text{C}_7\text{H}_{16}\text{O}_4$ ; this result was confirmed by the analysis of the silver salt, which has the composition  $\text{C}_7\text{H}_8\text{Ag}_2\text{O}_4$ .

This acid is, therefore, not hexamethylenedicarboxylic acid, the ethereal salt of which would have resulted from the action of pentamethylene dibromide on the sodium derivative of ethylic malonate, but it contains  $\text{CH}_2$  less than this acid, and is, therefore, probably pentamethylenedicarboxylic acid, the ethereal salt of which would be produced in the following manner.

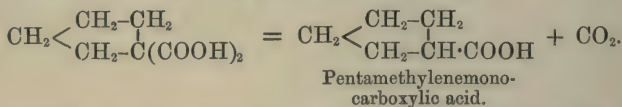
\* While this paper was in the press, it occurred to me that this formation of tetramethylene dibromide might be explained as follows. When trimethylene dibromide reacts with potassium cyanide, it may be assumed that the decomposition, to some extent, proceeds thus,



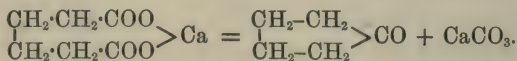
The cyanhydrin, thus produced, would then, on reduction, be converted into hydroxytetramethyleneamine,  $\text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{OH}$ , the hydrochloride of which, in contact with silver nitrite, would yield tetramethyleneglycol,  $\text{OH} \cdot [\text{CH}_2]_4 \cdot \text{OH}$ , tetramethylene dibromide being formed from this by the subsequent action of hydrogen bromide.—W. H. P., Jun.



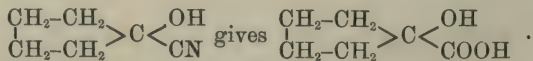
That the action actually takes place in this manner is proved by the following considerations. The bibasic acid of the formula  $\text{C}_7\text{H}_{10}\text{O}_4$  does not decolorise potassium permanganate in dilute alkaline solution; it is, therefore, a saturated acid, and must contain a closed carbon chain; when heated above its melting point, it rapidly decomposes, carbon dioxide being evolved and an oily acid produced, which distils constantly at  $214\text{--}215^\circ$ . The analysis of this acid and its silver salt prove that it is a monobasic acid of the formula  $\text{C}_6\text{H}_{10}\text{O}_2$ , and its formation, on the assumption that the bibasic acid was pentamethylenedicarboxylic acid, may be represented thus



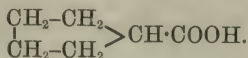
The properties of this monobasic acid coincide so exactly with those which could have been predicted for pentamethylenecarboxylic acid, that we had no hesitation in adopting this view of its constitution; curiously enough, however, while this research was in progress and nearing completion, Wislicenus and Gärtner (*Annalen*, **275**, 333) succeeded in preparing pentamethylenecarboxylic acid by a series of reactions which leave no doubt as to the constitution of their product. By the distillation of anhydrous calcium adipate, these chemists prepared, in the first place, the ketone of adipic acid (ketopentamethylene),



When this ketone is poured on to powdered potassium cyanide, and concentrated hydrochloric acid is added, the hydroxycyanide first produced is hydrolysed and converted into  $\alpha$ -hydroxypentamethylene carboxylic acid.



This hydroxy-acid is readily reduced by heating with hydriodic acid and phosphorus in a sealed tube at  $190\text{--}195^\circ$ , and is thus converted into pentamethylenecarboxylic acid,



The same acid was also obtained by converting ketopentamethylene

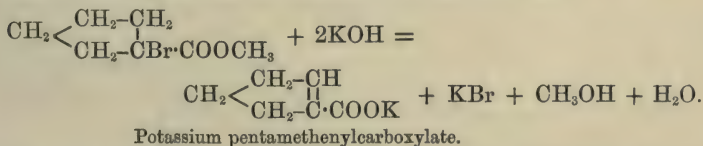


into pentamethylenic alcohol by reduction; the alcohol, when treated with hydriodic acid, yields the corresponding iodide, which, when digested with potassium cyanide, is converted into pentamethylenic cyanide; from this, pentamethylenecarboxylic acid is obtained by hydrolysis.

At our request, Professor Wislicenus was kind enough to send us a small quantity of his acid in order to enable us to decide definitely as to its identity with our acid. We converted his specimen into the acid chloride, from which we prepared the anilide,  $C_5H_9 \cdot CO \cdot NH \cdot C_6H_5$ , which crystallises from alcohol in a highly characteristic manner, and melts sharply at  $159-160^\circ$ . On repeating the experiment under precisely similar conditions, with our pentamethylenecarboxylic acid, we obtained an anilide which crystallised in the same characteristic manner, melted at  $159-160^\circ$ , and on careful comparison was found to be identical with the anilide of Wislicenus and Gärtner's acid.

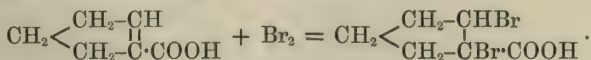
There can, therefore, be no doubt that the acid  $C_6H_{10}O_2$  obtained by us in the manner described above is in reality pentamethylenecarboxylic acid.

During the course of this investigation the action of bromine in the presence of phosphorous on pentamethylenecarboxylic acid was studied, and in this way some very interesting results were obtained. If the product is poured into methyl alcohol, methylic  $\alpha$ -bromopentamethylenecarboxylate, a colourless oil boiling at  $122-125^\circ$  (60 mm.), is produced; and this, when treated with aqueous potash, yields  $\Delta^1$ -pentamethenylcarboxylic\* acid.



This acid melts at  $119-121^\circ$ , and in many of its properties shows a marked resemblance to benzoic acid, from which, however, it is sharply differentiated by its instability towards alkaline permanganate solution, which it instantaneously decolorises.

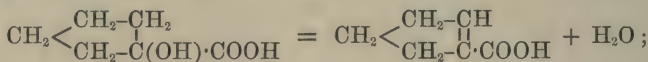
When subjected to the action of bromine vapour, pentamethenylcarboxylic acid is converted into a saturated dibromo-addition product,  $C_6H_8Br_2O_2$ ; this is evidently dibromopentamethylenecarboxylic acid produced according to the equation



\* This name is given to the acid in order to indicate its connection with the pentamethenyl derivatives described by Wislicenus and Gärtner (*Annalen*, **275**, 331)



By treating hydroxypentamethylenecarboxylic acid with hydriodic acid and phosphorus at  $150^{\circ}$ , Wislicenus and Gärtner (*loc. cit.*, p. 337) also obtained, in almost quantitative yield, an acid  $C_6H_8O_2$ , which melted at  $120^{\circ}$ , and was readily volatile with steam. There is no doubt that this acid is identical with pentamethylenecarboxylic acid, and its formation is readily understood, if it be assumed that the hydriodic acid of the strength employed acted simply as a dehydrating agent, thus,



the above mentioned chemists, indeed, discuss this possibility, but consider it very improbable that the reaction proceeds in this way without, however, giving any cogent reasons against this assumption; they are, moreover, unable to suggest any formula, other than the above, which corresponds with the properties of the acid.

The next step was to determine whether by the action of the mixed bromides on the sodium derivative of ethylic malonate any hexamethylene derivative had been formed. In order to decide this point, the various mother liquors of the pentamethylenedicarboxylic acid were evaporated to dryness and the residue was distilled. The colourless oily distillate, after treatment with permanganate to remove unsaturated compounds, was very carefully fractionated, and in this way rather more than 3 grams of a colourless acid, boiling at  $231-233^{\circ}$ , was obtained. It solidified in a freezing mixture, and on analysis gave numbers agreeing with the formula  $C_7H_{12}O_2$ , a result which was confirmed by the analysis of the silver salt,  $C_7H_{11}AgO_2$ .

That this acid is hexahydrobenzoic acid (hexamethylenecarboxylic acid),  $CH_2 < \begin{array}{c} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{array} > CH \cdot COOH$ , may be said to be clearly proved by the following facts:—

1. It has the same boiling point as Aschan's hexahydrobenzoic acid.

2. It is a saturated acid, since its solution in dilute sodium carbonate does not decolorise potassium permanganate.

3. The mixed dibromides from pentamethylenediamine undoubtedly contain considerable quantities of pentamethylene dibromide, as is proved by the synthesis of azelaic acid (see below), for the production of which the presence of this dibromide is necessary: as, therefore, this dibromide is present, it would be most remarkable if by its action on the sodium derivative of ethylic malonate, some ethylic hexamethylenedicarboxylate were not produced; and the latter, on hydrolysis and subsequent decomposition by heat, must yield hexahydrobenzoic acid (compare Freer and Perkin, *Trans.*, 1888, **53**, 206).

The formation of hexahydrobenzoic acid by this reaction is furthermore confirmed by Demjanoff, who (as he states in the description of his experiments which he kindly sent us) obtained an ethereal salt boiling at 244—255°, which, on hydrolysis, yielded a bibasic acid melting and decomposing at 145—160°; on analysis, it gave numbers agreeing with the formula of hexamethylenedicarboxylic acid,  $C_8H_{10}(COOH)_2$ .

Found, C = 55.6; H = 7.2. Theory, C = 55.8; H = 7.

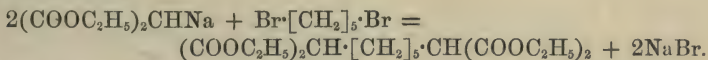
This bibasic acid, on distillation, yielded an oily monobasic acid, the calcium salt of which contained water of crystallisation, and, after drying, gave numbers agreeing with the formula  $(C_6H_{11}O_2)_2Ca$ :

Found, Ca = 13.6 per cent. Theory, 13.6 per cent.

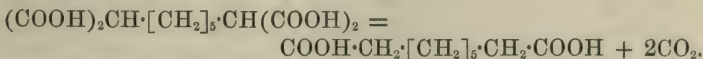
According to Aschan, the calcium salt of hexahydrobenzoic acid has the formula  $(C_6H_{11}O_2)_2Ca + 4H_2O$ . There can be no doubt that the latter was hexahydrobenzoic acid, and its synthesis from pentamethylene dibromide was, therefore, first accomplished by Demjanoff.

#### *Synthesis of Azelaic acid.*

When the product of the action of the mixed dibromides on the sodium derivative of ethylic malonate is fractionated, the temperature rises rapidly after the fraction 240—250°, which has just been described, has passed over, and if the distillation be continued under reduced pressure, a quantity of a thick oil is obtained, boiling at 270—275° (50 mm.). This oil, which constitutes about 25 per cent. of the product, is ethylic heptanetetracarboxylate, formed by the action of 1 mol. of pentamethylene dibromide on 2 mols. of ethylic sodiomalonate.



On hydrolysis with alcoholic potash, this ethereal salt yields an oily tetrabasic acid, which, when heated at 200°, is readily decomposed into carbon dioxide and a dark brown, crystalline acid. The latter crystallises from water in glistening plates, melts at 107°, and is in all respects identical with azelaic acid, as was clearly proved by a direct comparison with a sample of the latter obtained by the oxidation of Chinese wax. The synthesis of azelaic acid has not been accomplished previously, and its formation by the action of heat on heptanetetracarboxylic acid is readily understood with the aid of the following equation.



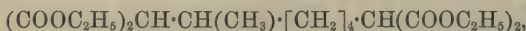
No trace of any other acid, suberic acid for example, was formed

in this reaction. It is very remarkable that tetramethylene dibromide and pentamethylene dibromide should differ so markedly in their behaviour towards ethylic sodiomalonate: that is, that pentamethylene dibromide should yield, besides ethylic hexamethylenedicarboxylate, also ethylic heptanetetracarboxylate, but that tetramethylene dibromide under precisely similar conditions should be quantitatively converted into ethylic pentamethylenedicarboxylate, without a trace of ethylic hexanetetracarboxylate,

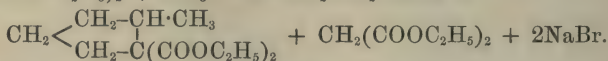


being formed.

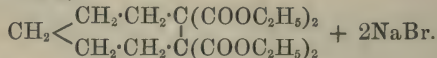
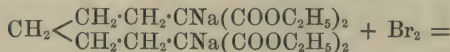
In connection with this point, it is interesting to note that methylpentamethylene dibromide,  $\text{CH}_3\cdot\text{CHBr}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Br}$ , and methyltetramethylene dibromide,  $\text{CH}_3\cdot\text{CHBr}\cdot[\text{CH}_2]_2\cdot\text{CH}_2\text{Br}$ , behave in a precisely similar manner when heated with ethylic sodiomalonate; the former (Freer and Perkin, *Trans.*, 1888, **53**, 202, 215) yielding ethylic methylhexamethylenedicarboxylate and considerable quantities of ethylic iso-octanetetracarboxylate,\*



whereas in the case of the latter (Colman and Perkin, *Trans.*, 1888, **53**, 185) ethylic methylpentamethylenedicarboxylate alone is formed.



As we were in possession of several grams of ethylic heptanetetracarboxylate, we studied the action of bromine on the disodium derivative of this ethereal salt, in order to determine whether it were possible in this way to accomplish a synthesis of a 7-carbon ring.



The product, on hydrolysis, gave an oily acid, which decomposed at  $200^\circ$ , carbon dioxide being evolved; the oily residue, after a time, deposited crystals of azelaic acid; unfortunately we were not able to isolate any other crystalline substance from the mother liquor of these crystals.

Experiments on the action of bromine on the disodium derivative of ethylic iso-octanetetracarboxylate which were instituted some time since by Freer and one of us (*loc. cit.*) gave a similar negative result. As, however, it has been shown (Kipping and Perkin, *Trans.*, 1891, **59**, 214—229; Wislicenus and Meyer, *Annalen*, **275**, 356—366)

\* Previously erroneously called ethylic isoheptanetetracarboxylate.



that a 7-carbon ring is capable of existence, it is very probable that if these experiments were repeated under different conditions a more satisfactory result would be attained.

The results of this research prove conclusively that the dibromide produced from the product of the action of silver nitrite on the hydrochloride of pentamethylenediamine contains, besides pentamethylene dibromide as its chief constituent, tetramethylene dibromide. It is, therefore, possible that the hydrocarbon obtained by Gustavson and Demjanoff (*Ber.*, **24**, 4002) by the action of sodium on these mixed dibromides, and which boiled at 35°, was not pure pentamethylene, as these chemists supposed, but a mixture of this hydrocarbon with tetramethylene.

Wislicenus and Hentzschel (*Annalen*, **275**, 327) prepared a hydrocarbon, which is probably pentamethylene, by reducing an alcoholic solution of pentamethylenic iodide,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ | \\ \text{CH}_2-\text{CHI} \end{smallmatrix}$ , with zinc and hydrochloric acid; it boiled at 50.25—50.75°, or about 15° higher than Gustavson and Demjanoff's product.

The boiling point of pentamethylene may be calculated in various ways, as for example, by subtracting the difference between the boiling points of heptamethylene (98—101°) and of hexamethylene (80°) from that of the latter the calculated boiling point being thus about 50°, a value agreeing with that found by Wislicenus and Hentzschel. It is, however, remarkable that the unsaturated hydrocarbon pentamethenylene,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2-\text{CH} \\ || \\ \text{CH}_2-\text{CH} \end{smallmatrix}$ , prepared by Wislicenus and Gärtner, which should boil higher than pentamethylene, was found to boil at 45°.

#### *Action of Silver Nitrite on Pentamethylenediamine Hydrochloride.*

Gustavson and Demjanoff (*J. pr. Chem.*, ii, **39**, 542), who first studied this decomposition, obtained as a result a substance boiling at 162° under a pressure of 30 mm., which they concluded was pentamethylene glycol,  $\text{C}_5\text{H}_{10}(\text{OH})_2$ ; by heating this with fuming hydrobromic acid in sealed tubes at 100°, they prepared a dibromide boiling at 204—206°, which, on analysis, gave numbers agreeing with the formula  $\text{C}_5\text{H}_{10}\text{Br}_2$ .

The yield of the glycol and bromide was, however, but small, 17 grams of the latter being obtained from 80 grams of pentamethylenediamine, whereas, according to theory, the yield should have been 180 grams. As it seemed likely that in the course of our experiments we should require considerable quantities of this dibromide, we made, in the first place, numerous experiments with the object of improving



the yield, using silver nitrite, sodium nitrite, free nitrous acid, &c., under a great variety of conditions, but the results were unsatisfactory. Ultimately, we found it best either to follow the method of Gustavson and Demjanoff exactly, or, in any case, to introduce only very slight modifications. The method of procedure finally adopted was the following:—To a fairly strong solution of pentamethylenediamine hydrochloride rather more silver nitrite was added than the amount required by theory. The nitrite was made into a thin paste with water and added little by little to the solution of the hydrochloride, the mixture being kept well cooled during the addition; care is necessary in performing this operation, as, owing to the evolution of nitrogen, the mixture froths very much, especially if the solution be too concentrated. Next day the mixture was heated on the water bath in a reflux apparatus for one hour; the precipitated silver chloride was then filtered off, washed with a little water, and the combined liquors concentrated by distillation in a flask connected with a fractionating column so as to prevent the glycol being carried over with the steam. In this operation, a small quantity of oil of very unpleasant odour passed over with the water, but was not obtained in quantity sufficient for further examination.

The residual liquid, after the bulk of the water had passed over, was made into a thick paste with anhydrous potassium carbonate, and the glycol which separated as an oil was removed by extracting six times with ether. On distilling off the ether, a considerable quantity of a brown oil remained, which was alkaline and smelt of ammonia. This was mixed with 10 times its volume of fuming hydrobromic acid (saturated at 0°), which at once acted on it, producing a hissing sound and dense, white fumes, a considerable amount of heat being generated. The mixture was heated on the water bath in a flask attached to a reflux condenser for about two hours, then resaturated with hydrogen bromide, sealed up in tubes, and heated in boiling water for four hours.

When cold, the contents of the tubes were poured into water, the heavy oily product extracted with ether, the ethereal solution washed with water and sodium carbonate solution, and dried over calcium chloride. On distilling off the ether, a dark brown liquid remained which had the odour characteristic of the higher dibromides in the fatty series. The bromine determination was made by Carius' method.

0.2398 gave 0.3925 AgBr.  $\text{Br} = 69.63$ .

$\text{C}_5\text{H}_{10}\text{Br}_2$  requires  $\text{Br} = 69.56$  per cent.

This result agrees closely with that obtained by Gustavson and Demjanoff, the mean of their analyses giving  $\text{Br} = 70.1$  per cent. In spite of the close agreement of the analytical numbers with

those required by the formula  $\text{Br}[\text{CH}_2]_5\text{Br}$ , the result of our subsequent experiments with this bromide proves that it is not by any means pure pentamethylene dibromide, but contains only approximately 25 per cent. of the latter, the remainder being tetramethylene dibromide,  $\text{Br}[\text{CH}_2]_4\text{Br}$ ; a mixture of this kind contains 72.89 per cent. of bromine.

As it is quite usual for a dibromide such as this, owing to slight decomposition and consequent loss of hydrogen bromide, to give numbers from 1 to 2 per cent. below the theoretical, it is not surprising that the numbers found in the present case are also inaccurate.

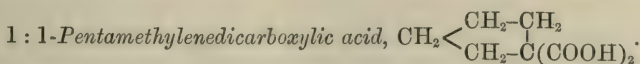
*Action of the Mixed Tetramethylene and Pentamethylene Dibromides on the Sodium Derivative of Ethylic Malonate.*

8 grams of sodium were dissolved in 100 grams of absolute alcohol, the solution well cooled, and a mixture of 40 grams of the bromide and 56 grams of ethylic malonate added. At ordinary temperatures, no change appears to take place except on long standing, but, on gently warming, the action soon begins, sodium bromide separates, and the liquid boils vigorously for some time; as soon as the reaction becomes sluggish, the mixture is heated on the water bath in a reflux apparatus for about two hours, allowed to cool, poured into twice its volume of water, and then extracted with ether four times. The ethereal solution is well washed with water to free it from alcohol, dried over calcium chloride, and the ether distilled off. Two experiments were made in this way, the total amount of bromide used being 90 grams.

The products from both these experiments were mixed and fractionated under reduced pressure (50 mm.), and in this way separated into three fractions boiling (1) between  $130^\circ$  and  $145^\circ$ ; (2) between  $155^\circ$  and  $180^\circ$ ; and (3) between  $180^\circ$  and  $275^\circ$ .

A small portion of fraction 2, which boiled at  $162\text{--}165^\circ$  under a pressure of 30 mm., was collected for analysis, but it did not give satisfactory numbers, owing to the fact that it contained traces of bromine.

The two fractions  $130\text{--}180^\circ$  were then mixed, and distilled under ordinary pressure, when they were separated into two parts, the one boiling below  $210^\circ$  and consisting almost entirely of ethylic malonate, the other a thick oil boiling at  $210\text{--}250^\circ$ . The further purification of fraction 3 boiling at  $180\text{--}285^\circ$  (50 mm.) will be described later (p. 104).



The fractions of the products of the action of the mixed bromides on ethylic sodiomalonate boiling at  $200\text{--}210^\circ$  and  $210\text{--}250^\circ$  cannot

be readily purified by fractional distillation, owing to the fact that the oil contains bromine which cannot readily be removed, and the presence of which renders the results of analysis valueless; for this reason, the oils were directly submitted to hydrolysis and the resulting acids further examined.

Fraction 200—210°, consisting principally of ethylic malonate, and weighing 37 grams, was mixed with a strong solution of 40 grams of pure caustic potash in methylic alcohol, and heated in a reflux apparatus for two hours. The alkaline solution was then diluted with water, evaporated on a water bath till free from alcohol, and the residue cooled, acidified with dilute sulphuric acid, and extracted five times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a small quantity of crude pentamethylenedicarboxylic acid, the malonic acid remaining almost entirely in the aqueous solution. This was subsequently worked up with the principal quantity obtained from the fraction 210—250°.

During the hydrolysis of the fraction 210—250°, weighing 55 grams, with 40 grams of potash dissolved in methylic alcohol, a considerable quantity of a crystalline potassium salt separated. The whole dissolved readily in water, and on evaporating, acidifying, and extracting with ether, as described above, 42 grams of a brown, oily acid was obtained, which, on standing over sulphuric acid in a vacuum, deposited crystals, and gradually became semi-solid. This crude product was spread on biscuit ware, and when the brownish, oily mother liquor had been entirely absorbed, the colourless, crystalline mass which remained was recrystallised several times from water. It then formed colourless prisms, which, on analysis, gave results agreeing with the formula of pentamethylenedicarboxylic acid,  $C_5H_8(COOH)_2$ .

0.1570 gave 0.3060  $CO_2$  and 0.0910  $H_2O$ . C = 53.16; H = 6.44.

0.1281 „ 0.2493 „ „ 0.0752 „ C = 53.08; H = 6.53.

$C_5H_8(COOH)_2$  requires C = 53.16; H = 6.33 per cent.

1:1-Pentamethylenedicarboxylic acid is readily soluble in hot, but comparatively sparingly in cold, water. It crystallises from water in colourless prisms, which, when heated in a capillary tube, melt at about 184—185°, undergoing decomposition into carbon dioxide and pentamethylenemonocarboxylic acid; this decomposition also takes place to some extent when the aqueous solution of the acid is evaporated, as the solution acquires a strong odour of the monocarboxylic acid. It is readily soluble in alcohol and ether, sparingly in benzene, and almost insoluble in light petroleum. The solution of this acid in sodium carbonate does not decolorise potassium permanganate, even on long standing, showing that the acid is saturated.

*Silver Salt of 1:1-Pentamethylenedicarboxylic acid.*—This was ob-



tained as a white, amorphous precipitate, on adding silver nitrate to a neutral solution of the ammonium salt of the acid; it is very sparingly soluble in water. After being well washed, it was dried over sulphuric acid in a vacuum and analysed.

0.2893 gave 0.2418  $\text{CO}_2$ , 0.0551  $\text{H}_2\text{O}$  and 0.1668 Ag.  $\text{C} = 22.79$ ;  
 $\text{H} = 2.11$ ;  $\text{Ag} = 57.66$ .

0.3157 gave 0.1816 Ag.  $\text{Ag} = 57.52$ .

$\text{C}_5\text{H}_8(\text{COOAg})_2$  requires  $\text{C} = 22.58$ ;  $\text{H} = 2.15$ ;  $\text{Ag} = 58.06$  per cent.

*Pentamethylenemonocarboxylic acid*,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH} \cdot \text{COOH} \end{array}$

When pure pentamethylenedicarboxylic acid is heated in a distilling flask, carbon dioxide is evolved, and an oil consisting of pure pentamethylenemonocarboxylic acid distils over constantly at  $214\text{--}215^\circ$ .

As the quantity of pure dicarboxylic acid at our disposal was small, we extracted, with ether, the biscuit ware containing the crude oily dicarboxylic acid (p. 97), evaporated the ethereal solution, and decomposed the brownish residue, by heating it at  $200^\circ$  until no more carbon dioxide was evolved. On distilling the residual oily acid, the whole (20 grams) passed over between  $210^\circ$  and  $230^\circ$  as a very unpleasant-smelling oily liquid which did not solidify when cooled in a freezing mixture. This acid is a mixture of pentamethylenedicarboxylic and hexamethylenedicarboxylic acids, the former being present in by far the larger quantity. The acids are, however, contaminated with some impurity which causes the alkaline solution to decolorise permanganate solution in the cold.

In order to remove this impurity, the mixed acids were dissolved in dilute sodium carbonate solution, cooled below  $0^\circ$ , and permanganate solution (1 per cent.) added until the pink colour was permanent. The excess of permanganate was then removed by adding a few drops of alcohol, the product filtered, and the filtrate evaporated to a small bulk. The acids were then liberated by adding dilute sulphuric acid, extracted with pure ether, and the ethereal solution, dried over calcium chloride, was evaporated. The residual oil (17 grams), submitted to very careful and repeated fractional distillation, gave about 9 grams of oil boiling constantly at  $214\text{--}215^\circ$  (the higher fraction is mentioned later), which, on analysis, gave results agreeing with the formula of pentamethylenemonocarboxylic acid.

0.1998 gave 0.4612  $\text{CO}_2$  and 0.1585  $\text{H}_2\text{O}$ .  $\text{C} = 62.95$ ;  $\text{H} = 8.80$ .

$\text{C}_5\text{H}_8\text{COOH}$  requires  $\text{C} = 63.16$ ;  $\text{H} = 8.77$  per cent.

The silver salt,  $\text{C}_6\text{H}_9\text{O}_2\text{Ag}$ , obtained by adding silver nitrate to a neutral solution of the ammonium salt, as a voluminous, white, amor-



phous precipitate, was well washed with water, dried over sulphuric acid in a vacuum, and analysed.

0.1496 gave 0.1778 CO<sub>2</sub>, 0.0582 H<sub>2</sub>O, and 0.0730 Ag. C = 32.41; H = 4.32; Ag = 48.79.

0.1872 gave 0.0908 Ag. Ag = 48.5.

C<sub>5</sub>H<sub>9</sub>COOAg requires C = 32.58; H = 4.07; Ag = 48.86 per cent.

The relative density, magnetic rotation, and refractive power determinations were carried out by Dr. W. H. Perkin, sen., who obtained the following results.

*Pentamethylenemonocarboxylic acid.*

The density determinations gave—

$d_{4^{\circ}/4^{\circ}}$	1.0540.	$d_{15^{\circ}/15^{\circ}}$	1.0452.
$d_{10^{\circ}/10^{\circ}}$	1.0489.	$d_{20^{\circ}/20^{\circ}}$	1.0416.
$d_{25^{\circ}/25^{\circ}}$	1.0385.		

The refractive power determinations gave—

$t.$	$\mu_A.$	$\mu_C.$	$\mu_D.$	$\mu_F.$	$\mu_G.$
17.7°	1.44759	1.45040	1.45280	1.45858	1.46314
	$\frac{\mu-1}{d}p.$				
	48.966	49.273	49.536	50.168	50.668

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
18.5°	0.9633	5.851
18.5	0.9708	5.896
18.5	0.9738	5.914
18.5	0.9669	5.873
18.5	0.9753	5.924
Average 18.5	0.9700	5.891

As in the case of all the saturated closed carbon chain carboxylic acids which have so far been examined, the magnetic rotation is very low.

*Pentamethylenecarboxylic Chloride, C<sub>5</sub>H<sub>9</sub>·COCl.*

This was prepared by heating the pure monocarboxylic acid (2 grams) with twice its volume of phosphorus trichloride for about 10 minutes, and after allowing the mixture to stand for about an hour, decanting the liquid from the layer of phosphorous acid, and submitting it to fractional distillation. As soon as the phosphorus trichloride had passed over, the thermometer rose rapidly to 160°,

between which temperature and  $162^{\circ}$  the whole distilled. This fraction was analysed by Carius' method.

0.1571 gave 0.1652 AgCl.  $\text{Cl} = 26.09$ .

$\text{C}_6\text{H}_9\text{OCl}$  requires  $\text{Cl} = 26.79$  per cent.

This chloride has a very similar smell, and is generally very similar in properties to the corresponding chloride of tetramethylenecarboxylic acid,

$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CH}_2-\text{CH}\cdot\text{COCl} \end{array}$ , which boils at  $139^{\circ}$ .

*Anilide of Pentamethylenecarboxylic acid*,  $\text{C}_5\text{H}_9\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ .—In order to prepare this, the chloride of pentamethylenecarboxylic acid was added drop by drop to a large excess of pure aniline, the whole being stirred with a glass rod during the operation. As soon as the vigorous action had moderated, the mixture was heated on a water bath for a few minutes, poured into water, and dilute hydrochloric acid added to dissolve the excess of aniline. The resulting crystalline precipitate was well washed with water, dried on a porous plate, recrystallised several times from alcohol, and analysed.

0.1975 gave 13.1 c.c. moist nitrogen at  $17^{\circ}$  and 762 mm.  $\text{N} = 7.71$ .

$\text{C}_5\text{H}_9\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 7.40$  per cent.

The anilide of pentamethylenecarboxylic acid crystallises from alcohol in magnificent glistening prisms, resembling sugar in appearance. It melts at  $159$ — $160^{\circ}$ , and when strongly heated distils apparently without decomposing. It is readily soluble in alcohol, benzene, chloroform, and acetic acid, less so in ether and light petroleum.

Professor Wislicenus was kind enough to send us a small quantity of pure pentamethylenecarboxylic acid prepared from the ketone of adipic acid (p. 89). In order to determine whether this was identical with our acid, we converted it into the acid chloride by treatment with phosphorus trichloride, and prepared from the fractioned chloride the anilide under exactly the same conditions as those given above. The anilide, after two crystallisations from alcohol, melted at  $159$ — $160^{\circ}$ , and gave the following results on analysis.

0.2200 gave 13.9 c.c. moist nitrogen at  $17^{\circ}$  and 766 mm.  $\text{N} = 7.39$ .

$\text{C}_5\text{H}_9\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 7.40$  per cent.

A very careful comparison of this product with the anilide obtained from our acid proved that the substances were identical.

*Methylic  $\alpha$ -Monobromopentamethylenecarboxylate,*

The action of bromine on pentamethylenecarboxylic acid was studied in the first instance, with the view of showing that, when treated in this way, the acid behaved as a saturated acid, forming a monobromo-substitution and not a dibrom-additive product. 5 grams of pentamethylenecarboxylic acid (b. p. 214—217°) was mixed with 0.3 gram of dry amorphous phosphorus in a flask connected with a reflux condenser, and 15 grams of dry bromine added in small portions at a time. The decomposition took place at once, quantities of hydrogen bromide being evolved. As soon as the violence of the action had moderated, the whole was heated on a water bath for five hours, the condenser then removed, and the heating continued until the excess of bromine had been driven off.

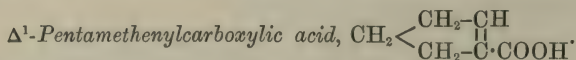
The dark-coloured product was converted into the methylic salt and not into the acid, as it was thought that the former would be more readily purified. For this purpose, the oil was added to excess of methylic alcohol, and after standing for an hour, the alcoholic solution was poured into water. The oily methylic salt was now extracted with ether, and the ethereal solution, after being well washed with water and dilute sodium carbonate solution, was dried over anhydrous potassium carbonate. On distilling off the ether, a dark brown oil was left, which, on being purified by fractionation under reduced pressure, yielded a colourless oil; this, on analysis, gave the following results.

0.3203 gave  $\text{AgBr} = 0.2960$ .  $\text{Br} = 39.3$ .

0.2326 „  $\text{AgBr} = 0.2165$ .  $\text{Br} = 38.8$ .

$\text{C}_6\text{H}_7\text{Br}\cdot\text{COOCH}$  requires  $\text{Br} = 38.8$  per cent.

*Methylic  $\alpha$ -bromopentamethylenecarboxylate* is a colourless oil which boils at 122—125° (60 mm.), and is specifically heavier than water. In its odour and general properties it closely resembles the corresponding tetramethylene derivative (Trans., 1892, **61**, 43).



This interesting unsaturated acid is formed when methylic monobromopentamethylenecarboxylate is acted on by aqueous potash, as explained in the introduction (p. 90). In order to prepare it, methylic monobromopentamethylenecarboxylate was mixed with strong potash solution (sp. gr. 1.2) and shaken from time to time until it had almost entirely dissolved, an operation which took about

two days. The solution was then heated to boiling for half an hour, cooled well, acidified, and extracted five times with pure ether. The ethereal solution was dried with calcium chloride, and evaporated, when a light brown oil was left, which, after a time, solidified almost entirely. The crystals were freed from oily impurity by spreading the mass on a porous plate, and recrystallising three times from water to which a little purified animal charcoal was added. In this way beautiful, colourless crystals were obtained.

0.1352 gave 0.3144  $\text{CO}_2$  and 0.0870  $\text{H}_2\text{O}$ .  $\text{C} = 64.22$ ;  $\text{H} = 7.25$ .

$\text{C}_6\text{H}_8\text{O}_2$  requires  $\text{C} = 64.28$ ;  $\text{H} = 7.14$  per cent.

The analysis and general properties of this acid, and especially its behaviour when treated with bromine (see below), leave scarcely any doubt that it is  $\Delta^1$ -pentamethenylcarboxylic acid. When heated in a capillary tube, the acid softens at about  $115^\circ$ , and melts not quite sharply at  $119$ – $121^\circ$ . It is readily soluble in hot water, alcohol, ether, and light petroleum, but only sparingly in cold water. It dissolves easily in alkalis and alkali carbonates, the cold solution in dilute sodium carbonate decolorising permanganate instantaneously, showing that the acid is unsaturated.

Pentamethenylcarboxylic acid crystallises from its solution in hot water or hot light petroleum in glistening plates, which very closely resemble benzoic acid in appearance. It is also remarkable that not only are the melting points of the two acids identical, but also that pentamethenylcarboxylic acid sublimes with great readiness even at  $100^\circ$  in very much the same way as benzoic acid. Pentamethenylcarboxylic acid is, without doubt, identical with the acid  $\text{C}_6\text{H}_8\text{O}_2$ , of which Wislicenus and Gärtner (*Annalen*, **275**, 337) obtained an almost quantitative yield by heating hydroxypentamethylenecarboxylic acid with feebly fuming hydriodic acid and phosphorus at  $150^\circ$  (see p. 91).

*Dibromopentamethylenecarboxylic acid*,  $\text{CH}_2 < \begin{array}{c} \text{CH}_2\text{-CHBr} \\ | \\ \text{CH}_2\text{-CBr-COOH} \end{array}$ .

In order to obtain further evidence in support of the view of the constitution of pentamethenylcarboxylic acid adopted in the preceding section, the action of bromine on this acid was carefully investigated. 0.06 gram of the pure acid was placed on a watch glass under a bell jar, and exposed to the action of bromine vapour for 10 hours; the excess of bromine was then removed by allowing the dark brown liquid product to remain over potash in a vacuum for 24 hours. In this way an almost colourless, crystalline mass was obtained, which, after recrystallisation from light petroleum, gave, on analysis, numbers agreeing with the formula of dibromopentamethylenecarboxylic acid.

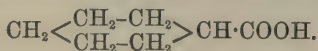


0.0984 gave 0.1358 AgBr. Br = 58.81.

$C_6H_8Br_2O_2$  requires Br = 58.82 per cent.

Dibromopentamethylenecarboxylic acid is readily soluble in ether, alcohol, chloroform, benzene, and hot light petroleum, sparingly so in the latter solvent in the cold, and almost insoluble in water. It crystallises from light petroleum in colourless leaflets, which, when heated in a capillary tube, soften at  $127^\circ$ , and melt at about  $134^\circ$ . A freshly prepared solution of the acid in sodium carbonate does not decolorise permanganate, but it does so after standing for some time owing to slight decomposition. When boiled with water, the acid first melts, and then dissolves completely, the solution now containing much hydrobromic acid.

*Hexamethylenemonocarboxylic acid (Hexahydrobenzoic acid),*



When crude pentamethylenedicarboxylic acid is distilled, and the oily distillate repeatedly fractioned, the principal product obtained is pentamethylenecarboxylic acid, boiling at  $214-215^\circ$ . But there is also a considerable quantity of a higher fraction, boiling between  $215^\circ$  and  $235^\circ$ ; this, when submitted to repeated and careful fractionation, gave about 3 grams of a colourless oil, which distilled between  $232^\circ$  and  $234^\circ$ . On analysis, it gave the following numbers.

0.1320 gave 0.3164  $CO_2$  and 0.1116  $H_2O$ . C = 65.37; H = 9.39.

$C_6H_{11} \cdot COOH$  requires C = 65.62; H = 9.38 per cent.

The silver salt of this acid was obtained as a white, amorphous precipitate on adding silver nitrate to the neutral solution of the ammonium salt; after washing it well with water, and drying over sulphuric acid in a vacuum, it was analysed.

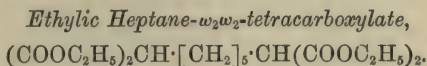
0.2010 gave 0.2613  $CO_2$ , 0.0868  $H_2O$ , and 0.0926 Ag. C = 35.45;

H = 4.79; Ag = 46.07.

$C_6H_{11} \cdot COOAg$  requires C = 35.74; H = 4.69; Ag = 45.95 per cent.

These results agree closely with those required for hexahydrobenzoic acid, and there is every reason to believe that the two are identical. Aschan (*Annalen*, **271**, 260), who prepared hexahydrobenzoic acid from benzoic acid, gives the boiling point of the former as  $232-233^\circ$ , and the melting point at  $28^\circ$ , and states that the acid does not decolorise potassium permanganate in dilute sodium carbonate solution. Our acid distilled at  $232-234^\circ$ , and was also indifferent to permanganate. When cooled in a freezing mixture, it solidified, but gradually liquefied again at ordinary temperatures. This difference in melting point is obviously due to the presence of some slight

impurity; but, owing to the small amount of material at our disposal, we were not able to remove it.



In fractioning the product of the action of the crude dibromides on ethylic sodiomalonate, a thick oil was obtained boiling at 180—285° (50 mm.), and from this, on redistilling, an almost colourless fraction boiling at 270—275° (50 mm.) was isolated. This, on analysis, gave the following results.

0.1758 gave 0.3754  $\text{CO}_2$  and 0.1291  $\text{H}_2\text{O}$ . C = 58.24; H = 8.16.

$\text{C}_{19}\text{H}_{32}\text{O}_8$  requires C = 58.76; H = 8.25 per cent.

This substance is ethylic heptane- $w_2w_2$ -tetracarboxylate, formed by the action of pentamethylene dibromide on 2 mols. of ethylic sodiomalonate, as explained in the introduction (p. 92).

It is an almost colourless oil which appears to undergo very slight decomposition when distilled under the ordinary pressure. When added to an ethereal solution of sodium ethoxide, a yellow, flocculent sodium derivative is precipitated; this probably has the constitution  $(\text{COOC}_2\text{H}_5)_2\text{CNa}\cdot[\text{CH}_2]_5\cdot\text{CNa}(\text{COOC}_2\text{H}_5)_2$ .

*Hydrolysis of Ethylic Heptanetetracarboxylate. Synthesis of Azelaic acid,  $\text{COOH}\cdot[\text{CH}_2]_7\cdot\text{COOH}$ .*

This ethereal salt was readily hydrolysed by boiling with excess of alcoholic potash, the action being complete after heating for half an hour on a water bath. In order to isolate the product, water was added, the solution evaporated on a water bath until free from alcohol, acidified, and extracted several times with pure ether. The ethereal solution after drying over calcium chloride and evaporating, deposited a thick, pale yellow oil, probably heptanetetracarboxylic acid; it did not crystallise, and therefore was not analysed.

When heated at 200°, this thick, oily acid readily decomposed, with evolution of carbon dioxide; the residual oil, which became nearly solid on standing, was readily purified by dissolving it in boiling water and decolorising by means of animal charcoal. Beautiful, colourless crystals separated from the hot concentrated solution as it cooled; after recrystallisation, it melted at 105—107°. Its identity with azelaic acid was established by a direct comparison with a sample of the latter, prepared by the oxidation of Chinese wax. The analysis gave the following results.

0.1102 gave 0.2301  $\text{CO}_2$  and 0.842  $\text{H}_2\text{O}$ . C = 57.03; H = 8.49.

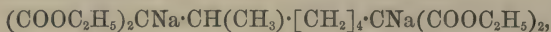
$\text{C}_9\text{H}_{16}\text{O}_4$  requires C = 57.44; H = 8.51 per cent.

The silver salt, prepared from the neutral solution of the ammonium salt by precipitating with silver nitrate, is a white, amorphous powder, and gave the following results on analysis.

- I. 0.1298 gave 0.1240  $\text{CO}_2$ , 0.0434  $\text{H}_2\text{O}$ , and 0.0686 Ag. C = 26.06; H = 3.75; Ag = 53.60.  
 II. 0.2296 gave 0.2232  $\text{CO}_2$ , 0.0740  $\text{H}_2\text{O}$ , and 0.1230 Ag. C = 26.53; H = 3.58; Ag = 53.57.  
 $\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$  requires C = 26.86; H = 3.48; Ag = 53.73 per cent.

*Action of Bromine on the Disodium Derivative of Ethylic Heptanetetracarboxylate.*

The action of bromine on the disodium derivative of ethylic iso-octanetetracarboxylate,



was studied by Freer and Perkin (Trans., 1888, 53, 220), with the object of preparing a heptamethylene derivative, but no such substance could be isolated; a similar want of success has attended our experiments on the action of bromine on the disodium derivative of ethylic heptanetetracarboxylate.

In carrying out this experiment, ethylic heptanetetracarboxylate (1 mol.) was mixed with an ethereal solution of sodium ethylate (2 mols.), and the calculated quantity of bromine (1 mol.) was gradually added, the whole being well agitated and cooled during the addition. The whole of the bromine disappeared, and the action was then evidently not at an end, as on adding iodine a considerable quantity of this was also absorbed; in fact, the action evidently proceeds in a very different way from that which takes place when the disodium derivatives of ethylic butane- and pentane-tetracarboxylate are acted on by bromine.

On hydrolysis, the product gave an oily acid, and this, when heated at  $200^\circ$ , yielded an oil from which a small quantity of a crystalline substance was obtained melting at  $106^\circ$ , and having all the properties of azelaic acid. The oily products were not further investigated.

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Owens College, Manchester.*

HEXAMETHYLENE DIBROMIDE AND ITS  
ACTION ON SODIUM AND ON ETHYLIC  
SODIOMALONATE.

BY

E. HAWORTH, B.Sc.,  
AND  
W. H. PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1894.]





## Hexamethylene dibromide and its action on sodium and on ethylic sodio-malonate.

By E. HAWORTH, B.Sc., and W. H. PERKIN, Jun.

AT the present time, little is known as to the existence and stability of closed carbon chains containing more than 6 carbon atoms.

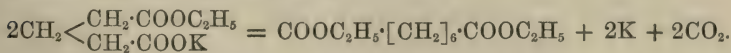
A substance containing an 8 or 9 carbon chain is not known to exist, but there is strong evidence that saturated compounds containing a ring of 7 carbon atoms, that is, derivatives of heptamethylene,

$\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , are not only capable of existence, but that they show a degree of stability which does not appear to fall short of that of the derivatives of tetra-, penta-, and hexa-methylene.

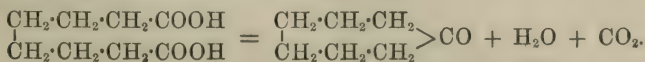
It is a well known fact that suberic acid, when distilled with lime, yields suberone,  $\text{C}_6\text{H}_{12}\text{CO}$  (Boussingault, *Annalen*, **19**, 308; Dale and Schorlemmer, *Ber.*, **7**, 806—808), and there can be little doubt that the constitution of this well characterised ketone must be represented by the formula  $\text{CO} < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , that it is, in fact, ketoheptamethylene.

Many reasons might be given in support of this view, but the following only need be mentioned here.

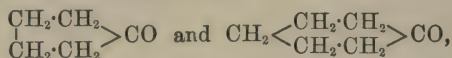
In the first place, the constitution of suberic acid has lately been proved by Crum Brown and Walker (*Annalen*, **261**, 119), who succeeded in synthesising the ethylic salt of this acid by submitting potassium ethylic glutarate to electrolysis.



Now in the formation of suberone from this acid, by the loss of water and carbon dioxide, the simplest way to represent the decomposition is obviously the following.



That the reaction really takes place in this way is rendered very probable by the recent work of Baeyer (*Annalen*, **278**, 110) and of Wislicenus and his pupils (*Annalen*, **275**, 309), the results of which show that the lower homologues of suberic acid, that is, adipic acid and pimelic acid, when distilled with lime, yield ketopentamethylene and ketohexamethylene respectively,

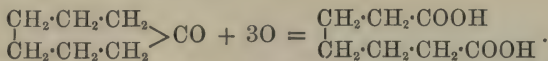


two ketones which, in their properties, show the closest resemblance to suberone.

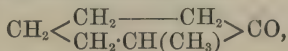
On oxidation, ketopentamethylene, ketohexamethylene, and suberone yield glutaric, adipic, and pimelic acids respectively, the acid in each case containing the same number of carbon atoms as the ketone from which it is derived.

As, in deciding the constitution of suberone, it is of the greatest importance to prove the constitution of the pimelic acid which this ketone yields on oxidation, Wislicenus and Mager (*Annalen*, **275**, 356) compared it very carefully with normal pimelic acid prepared from pentanetetracarboxylic acid (*Trans.*, 1887, **51**, 242), with the result that the acids, as had, indeed, been previously supposed, were proved to be identical.

Suberone must therefore be ketoheptamethylene, its oxidation to pimelic acid being represented thus—

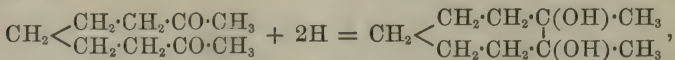


None of the other formulæ which have been proposed, such as, for example, that of methylketohexamethylene,



could yield normal pimelic acid on oxidation, unless, indeed, the oxidation be assumed to proceed in a very complicated manner.

Further evidence of the existence of heptamethylene compounds was obtained by Kipping and Perkin (*Trans.*, 1891, **59**, 214) in the course of their experiments on diacetylpentane. This diketone, when reduced, in moist ethereal solution, with sodium, yields as principal product dimethyldihydroxyheptamethylene according to the equation

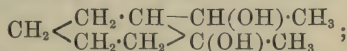


the reduction taking place in the same way as in the formation of pinacone from acetone.

This dihydroxy-compound, when heated with hydriodic acid and

amorphous phosphorus, yielded the corresponding hydrocarbon, dimethylheptamethylene,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_3 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_3 \end{smallmatrix}$ . The constitutions of these compounds are very fully discussed in the paper referred to, and there can scarcely be a doubt that the formulæ proposed best represent the reactions of the substances, which therefore must be regarded as derivatives of heptamethylene.

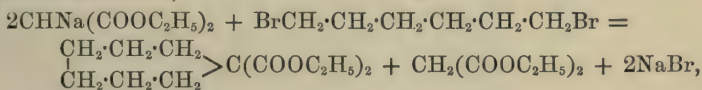
In a recent paper (*J. pr. Chem.*, **49**, 27), A. Michael considers it probable that the substance dimethyldihydroxyheptamethylene may have the constitution represented by the formula



but it is very difficult to see how such a compound could possibly be formed by the reduction of diacetylpentane, and this formula cannot, therefore, be accepted until some experimental proof of its accuracy has been deduced.

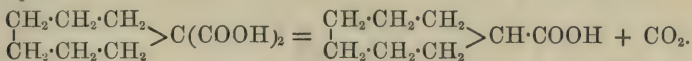
As suberone and dimethyldihydroxyheptamethylene are, so far, the only known substances which contain a 7-carbon ring, it appeared to us that it would be interesting to prepare other compounds of this class, and for this purpose it was thought best to employ the method which has been used with success in the formation of other closed carbon-chain compounds.

If the sodium compound of ethylic malonate be digested with hexamethylenedibromide, arguing from analogy, the reaction should proceed as follows,



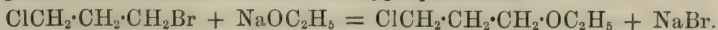
Ethylic 1 : 1-heptamethylenedicarboxylate.

and this ethereal salt, on hydrolysis, should yield the corresponding heptamethylenedicarboxylic acid, which, when distilled, would be converted into heptamethylenecarboxylic acid with loss of carbonic anhydride.



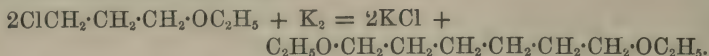
When these experiments were in contemplation, hexamethylene dibromide had not been prepared, and for a long time the attempts to obtain it were unsuccessful; ultimately, however, the following method was found to give satisfactory results.

$\omega\omega_1$ -Chlorobromopropene (trimethylenechlorobromide), when treated in alcoholic solution with sodium ethoxide (1 mol.), is readily decomposed with formation of chlorethoxypropane, thus—



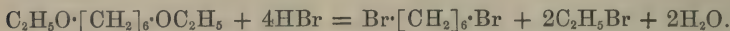


This, when acted on by sodium or potassium in ether, benzene, or light petroleum, undergoes condensation with formation of an oil of high boiling point, which evidently contains diethoxyhexamethylene, the reaction proceeding thus—



but the amount of this substance obtained is, unfortunately, very small.

Lastly, hydrobromic acid readily decomposes this compound, even at  $100^\circ$ , much more rapidly at  $150^\circ$ , with formation of hexamethylene dibromide.



Hexamethylene dibromide reacts very readily with the sodium compound of ethylic malonate, when the two are digested together in alcoholic solution, sodium bromide being precipitated and an oily substance formed; the latter was isolated in the usual manner, and then roughly separated into two parts by fractionation under reduced pressure (40 mm.), the fractions,  $130\text{--}220^\circ$  and  $220\text{--}290^\circ$ , being collected separately.

The fraction  $130\text{--}220^\circ$  (40 mm.), which contains a considerable quantity of regenerated ethylic malonate, was hydrolysed, and the resulting mixture of bibasic acids decomposed by heating at  $200^\circ$ , the residual oil being purified by repeated fractionation under ordinary pressures. In this way about 2 grams of a thick, colourless, unpleasant smelling oil was obtained; this boiled at  $248\text{--}250^\circ$ , and, on analysis, gave numbers agreeing with the formula of heptamethylenecarboxylic acid, which should have been produced if the reaction had proceeded as indicated above. The acid is a saturated compound, as its dilute alkaline solution does not decolorise potassium permanganate, and it very closely resembles pentamethylene- and hexamethylene-carboxylic acids in its properties, so that, although the amount of material at our disposal was not sufficient to allow of a careful examination of its salts, we think we are justified in assuming that the substance is heptamethylenecarboxylic acid.

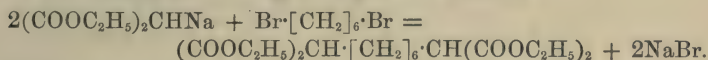
If this view be accepted, it is interesting to note that the series of monocarboxylic acids of the saturated closed carbon chains which have been synthetically produced, is complete up to and including 7 carbon atoms (see table next page).

It is remarkable that the difference in the boiling points of trimethylene- and tetramethylene-carboxylic acids should be so distinctly less than is the case between any other pair of consecutive acids.

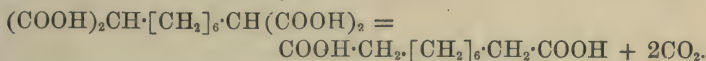
In fractioning the crude product of the action of hexamethylene dibromide on ethylic sodiomalonate, a considerable quantity of an

	B. p.	Diff.
Trimethylenecarboxylic acid, $\begin{array}{c} \text{CH}_2 \\   \\ \text{CH}_2 \end{array} > \text{CH} \cdot \text{COOH} \dots\dots\dots$	182°	13°
Tetramethylenecarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\   \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array} \dots\dots\dots$	195	20
Pentamethylenecarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\   \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{COOH} \dots\dots$	215	18
Hexamethylenecarboxylic acid, $\text{CH}_2 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\   \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{COOH}$	233	16
Heptamethylenecarboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\   \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{COOH}.$	249	

oily compound was obtained, which boiled at 277—280° under a pressure of 80 mm.; this, on investigation, proved to be ethylic octanetetracarboxylate, produced according to the equation—



This interesting substance, on hydrolysis, yields an oily acid, probably octanetetracarboxylic acid, which, when heated at 200°, is decomposed, with evolution of carbon dioxide and formation of sebacic acid, thus.

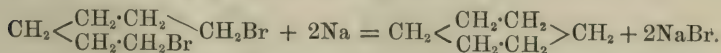


That sebacic acid is normal octane *ωω*-dicarboxylic acid, as represented in this equation, has been proved by Crum Brown and Walker (*Annalen*, **261**, 121), who obtained the acid synthetically by the electrolysis of potassium ethylic adipate,



and the formation of this acid from hexamethylene dibromide, proves, if any proof other than its synthesis were necessary, that this dibromide has the constitution  $\text{Br}[\text{CH}_2]_6\text{Br}$ , which has been assigned to it in this paper

While experimenting with hexamethylene dibromide, it was thought that it would be interesting to study the action of sodium on it, as it seemed probable that, in this way, hexamethylene (hexahydrobenzene) might be synthetically produced.



In carrying out the experiment, under conditions given in detail in this paper, a small quantity of a hydrocarbon was obtained, which

boiled at 77—80°, and, on analysis, gave numbers agreeing approximately with those required by the formula  $C_6H_{12}$ . The properties of this hydrocarbon agree closely with those ascribed by Baeyer (*Annalen*, **278**, 111) to hexamethylene, which he prepared by reducing hexamethylene iodide,  $CH_2<\overset{CH_2 \cdot CH_2}{\underset{CH_2 \cdot CH_2}{}}>CHI$ , with zinc dust and acetic acid, and which boils at 79°. It was our intention to repeat these experiments on a larger scale, in order, if possible, to obtain sufficient hydrocarbon to enable its physical constants to be determined and compared directly with those of hexamethylene; but we did not proceed further in this direction, as Salonina (*Ber.*, **26**, 2987) has intimated his intention of investigating this point.

*Chlorethoxypropane*,  $ClCH_2 \cdot CH_2 \cdot CH_2 \cdot OC_2H_5$ .

In order to prepare this substance, chlorobromopropane,  $Cl \cdot [CH_2]_3 \cdot Br$  (1 mol.), was dissolved in a little alcohol, and the calculated quantity of sodium (1 atom dissolved in 12 times its weight of absolute alcohol) added in three portions, the mixture being heated to boiling after each addition. As soon as the vigorous action had subsided, the product was cooled, mixed with twice its volume of water, and the oily layer extracted with ether; the ethereal solution was washed with water until free from alcohol, dried over calcium chloride, and the whole slowly distilled from a flask fitted with a fractioning column.

After the ether had passed over, a large quantity distilled between 40° and 60°, consisting, probably, principally of allylic chloride. The temperature then rose rapidly to 130°, between which and 135° the greater portion of the oil distilled; the residue, which contained unchanged chlorobromopropane, was used in a subsequent preparation. The fraction 130—135° was again distilled, and the portion boiling at 132—134° analysed, with the following result.

	Found.		Theory.
	I.	II.	
Cl.....	29.72	29.91 p. c.	$Cl \cdot [CH_2]_3 \cdot OC_2H_5$ . 28.97 p. c.

These analyses were made with different samples, and, from the results, it would appear that the chlorethoxypropane prepared in this way is not quite pure; a qualitative test showed that the oil contained traces of bromine, due, doubtless, to the presence of small quantities of bromethoxypropane.

A similar result was obtained by Gabriel (*Ber.*, **25**, 417), who, in preparing chlorophenoxypropane,  $Cl \cdot [CH_2]_3 \cdot OC_6H_5$ , from chlorobromopropane and sodium phenate, found that the product always contained traces of bromine.

*Chlorethoxypropane* is a colourless oil, which is specifically heavier than, and insoluble in water, and possesses a penetrating, disagreeable odour. As it appears to undergo a variety of interesting decompositions when treated with reagents, it is being subjected to careful investigation.

*Chloromethoxypropane*,  $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{O} \cdot \text{CH}_3$ , was prepared in a manner similar to the ethoxy-compound, sodium methoxide being employed instead of sodium ethoxide; it boils at 116—118°. Analysis.

	Found.	Theory. $\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{OCH}_3$ .
Cl. ....	33.7 per cent.	32.7 per cent.

The yield of the ethoxy-compound, obtained by the method described above, was about 40—45 per cent., that of the methoxy-compound about 50—60 per cent. of the theoretical; therefore, in the subsequent experiments, the latter was usually employed.

*Hexamethylene dibromide*,  $\text{BrCH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \text{Br}$ .

As explained in the introduction, the yield of this bromide obtained from chloromethoxypropane is very small, and a great many experiments were made, in the hope of discovering more favourable conditions, but without satisfactory results; the actual method which was ultimately adopted was the following.

20 grams of chloromethoxypropane was dissolved in about 60 c.c. of carefully purified light petroleum (b. p. 50—60°), in a flask connected with a long reflux condenser, and heated to boiling on a sand bath. The flame was removed, and then potassium gradually added in small pieces, the very violent action which takes place, accompanied by a hissing sound, being allowed to subside before each addition. The mixture soon begins to get thick, owing to the separation of potassium chloride and other salts; and when the potassium is no longer acted on, the whole is heated to boiling for half an hour, any unchanged metal being removed by the cautious addition of alcohol.

The product is then poured into water, the oily layer separated, washed with water, dried over calcium chloride, and carefully fractionated, the greater bulk passing over between 100 and 150° and containing unchanged chlorethoxypropane; this was used in a subsequent operation.

The residue in the retort, boiling above 150°, and consisting apparently, for the most part, of dimethoxyhexane,  $\text{CH}_3 \cdot \text{O} \cdot [\text{CH}_2]_6 \cdot \text{OCH}_3$ , was then digested in a reflux apparatus for three hours with an excess of fuming hydrobromic acid, the dark coloured product poured into water, the oily layer extracted with ether, dried over calcium chloride, the ether evaporated, and the residue heated in a sealed



tube with fuming hydrobromic acid for two hours at 150—160°. The product, which formed two layers, was poured into water, extracted as described above, and the crude, dark coloured bromide fractionated under reduced pressure (20 mm.); the principal portion, distilling between 125° and 140°, was used in the subsequent experiments.

A sample of the substance, boiling at about 137° (18—20 mm.), gave the following results, on analysis.

	Found.		Theory. Br(CH <sub>2</sub> ) <sub>6</sub> Br.
	I.	II.	
Br. ....	64·3	64·3 per cent.	65·5 per cent.

Hexamethylene dibromide is a heavy, colourless oil, which possesses the penetrating odour characteristic of the higher dibromides in the paraffin series; the pure substance distils with slight decomposition under the ordinary pressure. It is, doubtless, identical with the hexamethylene dibromide which Salonina (*Ber.*, **26**, 2987) obtained by heating hexamethyleneglycol diphenyl ether, C<sub>6</sub>H<sub>5</sub>O·[CH<sub>2</sub>]<sub>6</sub>·OC<sub>6</sub>H<sub>5</sub>, with fuming hydrobromic acid.

*Hexamethylene Glycol or ω<sub>1</sub>-Dihydroxyhexane*, CH<sub>2</sub>OH·[CH<sub>2</sub>]<sub>4</sub>·CH<sub>2</sub>OH.

This is produced when hexamethylene dibromide is boiled with dilute potassium carbonate solution. 15 grams of hexamethylene dibromide (b. p. 125—140° at 18 mm.) was boiled in a flask connected with a reflux condenser with 50 c.c. of water, small quantities of potassium carbonate being added from time to time; at the end of two days, the oily dibromide had completely passed into solution. The almost colourless liquid was then saturated with potassium carbonate, extracted 10 times with ether, the ethereal solution dried over anhydrous potassium carbonate, evaporated, and the residual thick oil submitted to distillation; almost the whole of it distilled between 230° and 240°, and, on refractioning, the pure glycol was obtained, boiling at 235—240°.

	Found.	Theory.
		OH·[CH <sub>2</sub> ] <sub>6</sub> ·OH.
C .....	60·85 per cent.	61·01 per cent.
H .....	11·83     „	11·86     „

Hexamethylene glycol is a colourless syrup, possessing a very faint odour and burning taste; it is miscible with water and alcohol, and distils under the ordinary pressure with very slight decomposition, thus showing no tendency to form an internal anhydride, as is the case with γ-pentylene glycol, CH<sub>3</sub>·CH(OH)·CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH (*Trans.*, 1887, **51**, 836).

*Action of Sodium on Hexamethylene Dibromide.*

10 grams of very finely divided sodium (prepared by agitating melted sodium under toluene) and about 50 c.c. of pure metaxylene was gently heated in a Würtz distillation flask connected with a water condenser, and then 20 grams of hexamethylene dibromide dissolved in 20 grams of metaxylene was added drop by drop from a dropping funnel; the action was sufficiently vigorous to keep the whole in rapid ebullition, and about 7 grams of a colourless oil distilled between 70° and 100°. The distillate was repeatedly fractioned over sodium, and in this way about 3 grams of a limpid liquid was obtained boiling at 77—80°; on analysis it gave the following results.

	Found.	Theory. $C_6H_{12}$ .
C .....	85.03 per cent.	85.71 per cent.
H .....	14.48     „	14.29     „

This hydrocarbon smells exactly like petroleum hexane, and is in all probability identical with the hexamethylene which Baeyer (*Annalen*, **278**, 111) prepared by reducing hexamethylene iodide with zinc-dust and acetic acid, and which boils at 79°.

*Action of Hexamethylene Dibromide on Ethylic Sodiomalonate.*

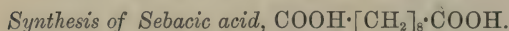
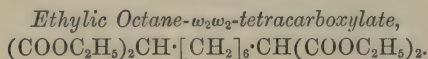
In studying this reaction, 3.9 grams of sodium was dissolved in 50 grams of absolute alcohol, and to the well-cooled solution a mixture of 26 grams of ethylic malonate and 20 grams of hexamethylene dibromide was added all at once. On gently heating the clear liquid in a reflux apparatus, the action set in as soon as the alcohol began to boil, and was sufficiently vigorous to keep the whole in ebullition for some minutes. After heating for half an hour, the product, which was only slightly yellowish, was cooled, mixed with water, and the oil which separated extracted three times with ether; the ethereal solution was washed well with water, dried over calcium chloride, and evaporated, and the residual oil (32 grams) fractionated under reduced pressure (40 mm.). In this way, the oil was roughly separated into two fractions boiling respectively at 130—220° (15 grams) and 220—290° (14 grams).

The lower fraction, which contained unchanged ethylic malonate, was hydrolysed by digesting with excess of alcoholic potash for one hour, the product mixed with water, evaporated till free from alcohol, acidified with sulphuric acid, and extracted five times with pure ether. The ethereal solution was dried over calcium chloride, the ether evaporated, and the syrupy residue, after it had been heated in a small distilling flask at 200° until the evolution of carbonic anhydride had ceased, was distilled. On repeatedly fractionating the

distillate, about 2 grams of an oily acid was obtained which distilled at 248—250°, and on analysis gave the following results.

	Found.		Theory.
	I.	II.	$C_8H_{14}O_2$ .
C .....	67.41	67.52 per cent.	67.60 per cent.
H .....	9.62	9.67 „	9.86 „

As explained in the introduction, this acid is probably heptamethylenecarboxylic acid; it is a saturated acid, as is shown by the fact that its solution in sodium carbonate does not decolorise permanganate. It is a colourless, disagreeably smelling oil, very sparingly soluble in water, but readily in solutions of the alkalis or alkali carbonates. Unfortunately, owing to the small amount of the acid at our disposal, we were unable to analyse any of its salts.



The portion of the oily product of the action of hexamethylene dibromide on ethylic sodiomalonate which boils at 220—290° (40 mm.), consisting principally of ethylic octanetetracarboxylate, was carefully fractionated, and the fraction 277—280° (40 mm.) analysed with the following result.

	Found.	Theory. $C_{20}H_{34}O_8$ .
C .....	58.52 per cent.	59.70 per cent.
H .....	8.74 „	8.46 „

The oil unfortunately contained small quantities of bromine, which accounts for the slight deficiency in carbon and hydrogen in the above analysis; there can, however, be no doubt, from the behaviour of this ethereal salt on hydrolysis, that its constitution is represented by the formula given above. Ethylic octanetetracarboxylate is a very thick, almost colourless oil which, even after standing for some days, showed no signs of crystallising. The crude ethereal salt boiling at 270—285° (40 mm.) was hydrolysed by boiling with a large excess of alcoholic potash for two hours in a reflux apparatus, the product was freed from alcohol by evaporating to dryness, dissolved in water, acidified, and extracted five times with pure ether.

The syrupy residue left on evaporating the carefully-dried ethereal solution, and which probably consisted of octanetetracarboxylic acid, was not analysed, but converted at once into sebacic acid by heating at 200° until the evolution of carbonic anhydride had ceased. The dark-coloured oil solidified on cooling to a mass of crystals, which

were first freed from oily mother liquor by spreading on a porous plate, and then repeatedly recrystallised from formic acid with the aid of animal charcoal. In this way, colourless, nodular masses of crystals were obtained which melted at 125—127°, and gave the following results on analysis.

	Found.	Theory. $C_{10}H_{18}O_4$ .
C .....	59.45 per cent.	59.40 per cent.
H .....	8.94 „	8.91 „

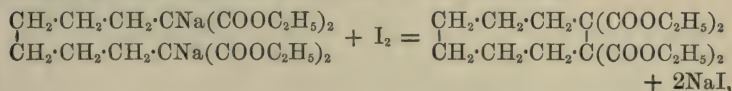
The silver salt was prepared by precipitating a neutral solution of the ammonium salt with silver nitrate; the white, sparingly-soluble, flocculent precipitate, after washing well and drying at 100°, gave the following results on analysis.

	Found.	Theory. $C_{10}H_{16}Ag_2O_4$ .
C .....	29.20 per cent.	28.84 per cent.
H .....	4.04 „	3.84 „
Ag .....	51.56 „	51.92 „

That this acid is sebacic acid was proved by carefully comparing it with a sample of this acid prepared from castor oil; both specimens melted at the same temperature, and were exactly similar in all other respects.

*Action of Sodium Ethoxide and Iodine on Ethylic Octanetetracarboxylate.*

Ethylic octanetetracarboxylate contains two CH groups, each of which is connected with two  $COOC_2H_5$  groups, and it should therefore, when treated with sodium ethoxide, form a disodium compound; the latter, by the action of iodine, might be expected to yield the ethylic salt of octomethylenetetracarboxylic acid thus—



just as ethylic butane-tetracarboxylate and ethylic pentane-tetracarboxylate, under similar conditions, yield the corresponding tetramethylene and pentamethylene derivatives. In order to test this, 1.2 grams of sodium was dissolved in 5 grams of absolute alcohol, 10 grams of ethylic octanetetracarboxylate dissolved in about 50 c.c. of pure ether added, when a sticky sodium compound separated out and adhered firmly to the bottom of the flask containing the mixture; 6.3 grams of iodine dissolved in ether was then poured in in small quantities at a time, and this, on shaking, was rapidly decolorised; indeed, in order to obtain a permanent coloration, it was found necessary to add 6 grams more of iodine. The product was mixed



with water, the dark-coloured ethereal solution separated, and washed with a little sodium bisulphite, but it was found that as soon as the solution had become colourless it rapidly began to turn brown again, evidently owing to separation of iodine. The ethereal solution was therefore separated, dried over calcium chloride, and evaporated, when 14.5 grams of a dark brown oil remained containing much iodine. This was hydrolysed by boiling with excess of alcoholic potash, and the product, after the removal of alcohol by evaporation, dissolved in water and acidified with hydrochloric acid; this caused the precipitation of a yellowish, semi-crystalline mass, which was collected, washed with water containing sulphuric acid, and recrystallised from formic acid. In this way, a considerable quantity of a colourless, crystalline acid was obtained which melted at about  $125^{\circ}$ , and, on analysis, proved to be sebacic acid.

	Found.	Theory. $C_{10}H_{18}O_4$ .
C .....	59.41 per cent.	59.40 per cent.
H .....	9.10 „	8.91 „

Similar results were obtained in attempting to prepare derivatives of heptamethylene from ethylic heptanetetracarboxylate (Trans., 1894, 55, 105) and from ethylic isooctanetetracarboxylate (Trans., 1888, 53, 220), in all cases much more than the calculated quantity of halogen was required before the action was complete, and the products of the reaction, on hydrolysis, gave acids derived from the unchanged ethereal salts and not derivatives of closed carbon chains.

It is very difficult to understand what actually takes place in these reactions.

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*CIS- AND TRANS-HEXAHYDRO-ORTHOTOLUIC*  
ACIDS.

BY

W. GOODWIN

AND

W. H. PERKIN, JUN.

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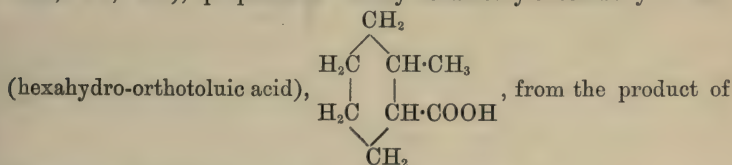
[From the Transactions of the Chemical Society, 1895.]



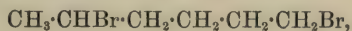
# cis- and trans-Hexahydro-orthotoluic acids.

By W. GOODWIN and W. H. PERKIN, jun.

SOME time since, one of us, in conjunction with P. C. FREER (Trans., 1888, 53, 208), prepared a methylhexamethylenecarboxylic acid



the action of methylpentamethylene dibromide,



on the sodium derivative of ethylic malonate, and described it as a colourless oil boiling at 235—236°.

Recently Markownikoff (*J. pr. Chem.*, 1894, 49, 65) has studied the reduction products of orthotoluic acid, obtained by treating a boiling solution of the acid in amylic alcohol with a large excess of sodium, and has isolated a hexahydro-orthotoluic acid, which boils at 240°, and solidifies readily on cooling, the pure acid melting at 50—52°; no mention whatever is made of the work of Perkin and Freer, the author being apparently ignorant of its existence.

The wide difference in properties between the synthetical acid and the acid obtained by reduction made it desirable that the whole subject should be reinvestigated, with a view of determining whether these acids are in reality isomeric, and if so, what the nature of the isomerism is; with this object in view, we, in the first place, prepared Markownikoff's acid, following this author's directions as closely as possible.

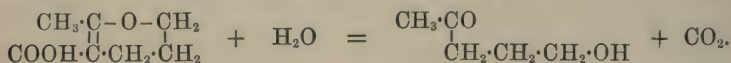
As the result of a careful examination of this acid, we are able to confirm his description of its properties in every particular. Perhaps the most important property, in view of the present question of



isomerism, is the ease with which the acid solidifies after distillation, even when not quite pure. We prepared also the anilide of the acid,  $C_7H_{13} \cdot CO \cdot NH \cdot C_6H_5$ , which has not hitherto been described, in order to compare it with the anilide of the synthetical acid; it crystallises beautifully from light petroleum, and melts at  $148^\circ$ .

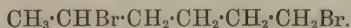
In discussing the question of the isomerism of these two acids, it will be necessary to show, in the first place, that the acid described by Freer and Perkin is a hexahydro-orthotoluic acid, and therefore *structurally identical* with Markownikoff's acid, and, in order to do this, it will be well to give briefly the method by which it was synthesised.

The starting point in the synthesis is acetobutylic alcohol. This is prepared by digesting methyldehydrohexonecarboxylic acid with water as long as carbon dioxide is evolved (Trans, 1889, **51**, 718), when the following decomposition takes place.

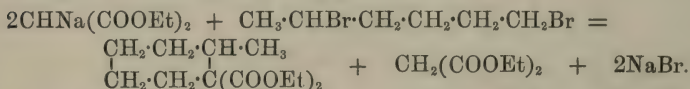


That the ketonic alcohol obtained is, in reality, acetobutylic alcohol, is proved by its behaviour on oxidation; chromic acid converting it, in the first place, into acetobutyric acid,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , which, on further oxidation, yields acetic and succinic acids (*loc. cit.*, p. 719).

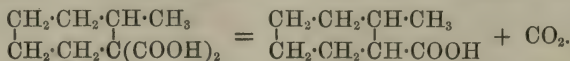
Acetobutylic alcohol is readily reduced by sodium amalgam, forming  $\delta$ -hexylene glycol  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , from which, by the action of fuming hydrobromic acid,  $\delta$ -hexylene dibromide is obtained; the latter, judging from the manner in which it is formed, evidently must be represented by the formula



If, now, the sodium derivative of ethylic malonate be digested with this dibromide, an action will take place readily, ethylic methylhexamethylene dicarboxylate being produced thus



This ethereal salt, on hydrolysis, yields the corresponding dibasic acid, which, when distilled, is decomposed with formation of methylhexamethylenecarboxylic acid or hexahydro-orthotoluic acid.



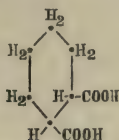
If this synthesis be carefully considered, it is difficult to see how the acid obtained can possibly have any other constitution than that

of a hexahydro-orthotoluic acid; unless, indeed, it be an unsaturated acid. This alternative has already been discussed (Trans., 1888, 53, 208), and it was shown that the magnetic rotation of the acid clearly proves that it cannot be unsaturated; this has since been confirmed by the discovery that the sodium salt of the acid does not decolorise potassium permanganate (Baeyer, *Annalen*, 1888, 245, 148).

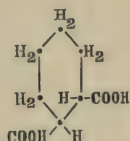
The anilide of the synthetical acid,  $C_7H_{13}CO \cdot NH \cdot C_6H_5$ , melts at  $66-68^\circ$ , and differs in its properties widely from the anilide obtained by Markownikoff, which, as already stated, melts at  $148^\circ$ .

From the above statement it must be assumed that the synthetical acid and Markownikoff's hexahydro-orthotoluic acid are structurally identical; obviously then the cause of the well-marked isomerism must be sought in other than purely chemical reasons.

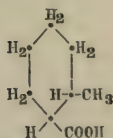
A careful examination of the formula of hexahydro-orthotoluic acid indicates at once that this acid, like hexahydrophthalic acid, may exist in two stereoisomeric modifications



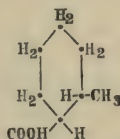
*cis*-Hexahydrophthalic acid.



*trans*-Hexahydrophthalic acid.

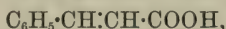


*cis*-Hexahydro-orthotoluic acid.



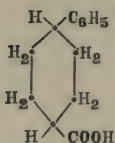
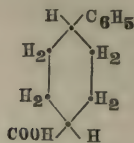
*trans*-Hexahydro-orthotoluic acid.

The two modifications of hexahydrophthalic acid (Baeyer, *Annalen*, 1890, 258, 169) are well defined, and it is improbable that the substitution of a methyl or other alkyl group for one carboxyl group in this acid would greatly affect the conditions of isomerism, because crotonic acid,  $CH_3 \cdot CH : CH \cdot COOH$ , and cinnamic acid,



which are derived from fumaric acid in this way, exist in stereoisomeric forms.

In connection with this point, it is interesting to note that Baeyer and Rassow (*Annalen*, 1894, 282, 139) have lately shown that paraphenylhexahydrobenzoic acid, like hexahydroterephthalic acid, exists in two well-defined stereoisomeric modifications which melt at  $111-113^\circ$  and  $202^\circ$  respectively.

*cis-p*-Phenylhexahydrobenzoic acid.*trans-p*-Phenylhexahydrobenzoic acid.

These acids are partially convertible into one another by heating with hydrochloric acid; in any case, whether the acid of high melting point or of low melting point is used in the experiment, a condition of equilibrium results, when the product contains 90 per cent. of the former and 10 per cent. of the latter.

In order to show, if possible, that the difference in properties between the two hexahydrotoluic acids was due to stereoisomerism, each was heated with hydrochloric acid at 200°, but without any apparent change, as the solid acid after this treatment and subsequent refractionation again solidified almost completely, and the liquid acid after similar treatment, even when allowed to remain for some time at -10° in contact with a crystal of the solid acid, showed no signs of crystallisation. The same result was always obtained whenever the acids were heated, either with hydrochloric acid or with quinoline, at various temperatures and under various conditions.

Ultimately it was found that the solid acid, although crystallising with such facility when pure, if mixed with small quantities of the liquid acid, does not solidify at all at -10°, and therefore if, in the above experiments, a partial change of the one isomeride into the other had taken place, the detection of the change by freezing experiments would scarcely be possible; the conversion of the liquid acid into the solid acid was ultimately proved to have taken place in the following manner. A small quantity of the liquid acid which had been twice heated with hydrochloric acid at 200°, and subsequently boiled with quinoline for two days, was converted into the acid chloride by means of phosphorus pentachloride, and from this the anilide was prepared. The crystalline product showed no definite melting point, but on repeated treatment with small quantities of cold ether, the melting point gradually rose until ultimately the residual colourless substance melted at 143—145°, and consisted of the nearly pure anilide of the solid acid, which, as stated above, melts at 148°.

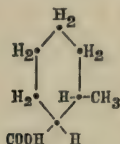
This anilide was now decomposed by heating with hydrochloric acid, and the regenerated acid distilled; on cooling, the distillate at once solidified, in the manner characteristic of the solid acid, and, after purification, the crystals melted at 47—49° instead of at 50—52°.

It is clear, then, that hexahydro-orthotoluic acid exists in two stereo-

isomeric forms, and that the liquid modification obtained by synthesis, when treated as described above, is converted into the solid modification obtained by Markownikoff by the reduction of orthotoluic acid. It is of course not possible to be certain which of the agents used actually brought about the change; in all probability it was due to the action of the hydrochloric acid, but this is a matter of small importance.

There is some reason for believing that the solid acid also is, to a small extent, converted into the liquid acid by treatment with hydrochloric acid, as the product after fractionation melts below  $30^{\circ}$ , due to the crystals containing a small quantity of an oily substance, which is readily removed in contact with porous porcelain; the quantity converted, however, is certainly very small. As the solid acid is much more stable towards hydrochloric acid than the liquid acid, it is probably the *trans*-modification, the latter being the *cis*-modification; and this method of distinguishing the isomerides has been adopted in the following pages.

*trans-Hexahydro-orthotoluic acid.*



Markownikoff (*J. pr. Chem.*, 1894, **49**, 65) prepared this acid by reducing orthotoluic acid in boiling amylic alcohol solution with excess of sodium. As considerable quantities of this acid were required for the experiments described in this paper, about 100 grams of pure orthotoluic acid were reduced in portions of 25 grams at a time, each quantity being four times treated with sodium and amylic alcohol, the details of the operations being the same as recommended by Markownikoff.

On fractionating the combined products, a considerable quantity passed over below  $200^{\circ}$ , the thermometer then rose rapidly to  $230^{\circ}$ , and between this temperature and  $245^{\circ}$  the whole distilled as a colourless oil, which solidified on standing.

The crystals, after being freed from oily matter by contact with porous porcelain, were purified by treatment with permanganate and recrystallisation from benzene, as recommended by Markownikoff; the colourless, crystalline product melted at  $50-52^{\circ}$ , and, on analysis, gave the following results.



	Found.			Theory. $C_8H_{14}O_2$ .
	I.	II.		
C.....	67.55	67.40	per cent.	67.61 per cent.
H.....	9.89	9.86	„	9.86 „

This acid has all the properties ascribed to it by Markownikoff; it boils at 240—241°, and, excepting for the facility with which it crystallises at ordinary temperatures, it resembles closely the *cis*-acid, which boils at 236.5—237°.

*Anilide of trans-hexahydro-orthotoluic acid*,  $C_7H_{13} \cdot CO \cdot NH \cdot C_6H_5$ .

In order to prepare this substance for comparison with the anilide of the *cis*-acid, the pure *trans*-acid was digested in a reflux apparatus with excess of pure aniline for three days. The product, which contained a quantity of crystals, was dissolved in ether, and the ethereal solution after being washed, first with dilute hydrochloric acid and then with sodium carbonate, was dried over anhydrous potassium carbonate and evaporated; the residue, which rapidly solidified, was spread on a porous plate, and subsequently recrystallised from a mixture of benzene and light petroleum, with the aid of animal charcoal. After repeated recrystallisation, the melting point remained constant at 148° and the following results were obtained on analysis.

	Found.	Theory. $C_{14}H_{19}NO$ .
N.....	6.59 per cent.	6.45 per cent.

The anilide of *trans*-hexahydro-orthotoluic acid crystallises from a mixture of benzene and light petroleum in glistening plates with a slight, bluish fluorescence, somewhat similar to, but much less pronounced than that of anthracene crystals. It is sparingly soluble in ether and light petroleum, readily in alcohol or benzene, but insoluble in water; when heated in small quantities, it distils without decomposition.

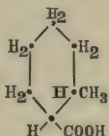
As it appeared possible that, in reducing orthotoluic acid, the *cis*-acid might have been formed along with the *trans*-acid, the liquid products of the action, which are always present in considerable quantity, were carefully investigated; the porous plate, which had been used in the purification of the *trans*-acid, was extracted with ether in a Soxhlet apparatus, and the combined acids submitted to careful fractionation in a Würtz flask fitted with a long neck.

In this way, a disagreeably smelling acid was obtained, which boiled at 176°, and consisted of nearly pure isovaleric acid.

	Found.	Theory. $C_4H_9 \cdot COOH$ .
C.....	59.45 per cent.	58.82 per cent.
H.....	9.87 „	9.80 „

This acid is probably produced by the oxidation of the sodium isoamylate formed during the above reduction, and is apparently always present in small quantity in the products of similar reductions, as both Rassow and Markownikoff observed the presence of a disagreeably smelling acid in their products. As soon as the valeric acid had passed over, the temperature rose rapidly to  $235^{\circ}$ , and the distillate boiling at  $235\text{--}245^{\circ}$  again became almost solid. The oily matter removed from the crystals, as before, on further purification, also solidified, so that apparently the only product of the reduction of orthotoluic acid by sodium and amylic alcohol is *trans*-hexahydro-orthotoluic acid.

*cis*-Hexahydro-orthotoluic acid (*Methylhexamethylenecarboxylic acid*).



The method adopted in preparing this acid was similar to that employed by Freer and Perkin (*Trans.*, 1888, **53**, 206), one or two slight modifications being introduced in purifying the product.

Ethylic methylhexamethylene dicarboxylate was first synthesised by heating methylpentamethylene dibromide (115 grams) with ethylic malonate (160 grams) and sodium ethoxide (23 grams of sodium) in a reflux apparatus for 10 hours. The ethereal salt, isolated in the usual manner, was carefully fractioned, and the portion boiling at  $260\text{--}265^{\circ}$ , and which, as before, contained traces of bromine, hydrolysed by boiling it with twice the calculated quantity of alcoholic potash for five hours. The product, freed from every trace of alcohol by repeated evaporation with water, was cooled, acidified, and extracted three times with ether which had been purified by repeated distillation over sodium; the ethereal solution was then dried over calcium chloride, evaporated, and the oily residue allowed to stand in a cool place for six weeks, over sulphuric acid in a vacuum. At the end of that time, the crystals were collected by means of the pump, freed completely from the thick, oily, mother liquor by contact with porous porcelain, and then recrystallised twice from water. An analysis showed that the crystals were pure methylhexamethylene dicarboxylic acid.

	Found.	Theory. $C_9H_{14}O_4$ .
C.....	58.10 per cent.	58.06 per cent.
H.....	7.68 „	7.53 „

Methylhexamethylenedicarboxylic acid melts at about  $147^{\circ}$ , and, although its properties have already been given (*loc. cit.*, p. 208), we may here add that the solution of the sodium salt does not decolorise permanganate, thus precluding the possibility of the acid being unsaturated.

In order to obtain the monocarboxylic acid, the pure dibasic acid was distilled, and the oily distillate carefully fractioned; the greater portion boiled at  $236.5\text{--}237^{\circ}$  (the boiling point previously given was  $235\text{--}236^{\circ}$ ); but all attempts to obtain this acid in a crystalline condition by leaving it in a freezing mixture in contact with a crystal of the *trans*-acid were fruitless.

On testing the acid with permanganate in alkaline solution, a slight action was noticed; in order, therefore, to still further purify the product, it was dissolved in a dilute solution of sodium carbonate, cooled with ice, excess of permanganate added, and the mixture allowed to stand for half an hour. The permanganate was then destroyed by alcohol, the liquid filtered, evaporated nearly to dryness, and the acid isolated and fractioned as before; it again boiled constantly at  $236.5\text{--}237^{\circ}$ , but, on cooling, showed no signs of crystallising.

On analysis it gave numbers agreeing closely with those required by the formula of hexahydro-orthotoluic acid.

	Found.		
	I.	II.	
C.....	67.52	67.50 per cent.	Theory. $C_8H_{14}O_2$ . 67.61 per cent.
H.....	9.81	9.92 „	9.86 „

These analyses were carried out with the products from two distinct preparations.

*Anilide of cis-hexahydro-orthotoluic acid*,  $C_7H_{13}\cdot CO\cdot NH\cdot C_6H_5$ .—This characteristic derivative was prepared by boiling the purified acid with a considerable excess of aniline for three days in a reflux apparatus; the dark coloured product was dissolved in ether, and after being washed well, first with dilute hydrochloric acid and then with sodium carbonate solution, it was dried over anhydrous potassium carbonate, evaporated, and the residual brownish oil allowed to stand over sulphuric acid in a vacuum until it had completely solidified.

This product differs in its properties in a marked manner from the corresponding anilide of the *trans*-acid, it has little facility for crystallising, and separates from most solvents in the form of an oil. The best way of purifying it is to dissolve the dark coloured, crystalline mass in a large quantity of boiling light petroleum (b. p.  $50\text{--}60^{\circ}$ ), and after digesting the solution with purified animal charcoal until the

colour becomes pale yellow, to filter and allow the solution to evaporate at the ordinary temperature, when the anilide rapidly separates in long, colourless, silky needles. These crystals were collected, re-crystallised from light petroleum, and analysed with the following result.

	Found.	Theory. $C_{14}H_{19}NO$ .
N.....	6.43 per cent.	6.45 per cent.

The anilide of *cis*-hexahydro-orthotoluic acid melts at 66—68°. It is readily soluble in ether, alcohol, chloroform, and benzene, very sparingly in cold light petroleum, and almost insoluble in water. When rapidly heated in small quantity, it distils apparently without decomposition, yielding an oily distillate, which solidifies only very slowly, even in contact with a crystal of the pure substance.

*Conversion of cis-Hexahydro-orthotoluic acid into trans-Hexahydro-orthotoluic acid.*

As explained in the introduction, considerable difficulty was experienced in experimentally proving this isomeric change, owing to the fact that small quantities of the oily *cis*-acid are sufficient to prevent the solid *trans*-acid from crystallising even when the mixture is cooled to  $-10^{\circ}$ .

In the first experiments, the pure *cis*-acid was heated with concentrated hydrochloric acid in a sealed tube for five hours at 190—200°, the slightly brownish product was poured into water, and the oily acid extracted with ether; the ethereal solution was dried over calcium chloride and fractionated, when the whole distilled between 236° and 238° as a colourless oil, which, even at  $-10^{\circ}$ , in contact with a crystal of the *trans*-acid, showed no signs of crystallisation. This same sample was then again heated with hydrochloric acid, but even after this second treatment it did not crystallise. The acid was then boiled with four times its volume of pure quinoline in a reflux apparatus for three days, the product digested with hydrochloric acid, and distilled in a current of steam; the distillate was extracted with ether, and the acid distilled, when again the whole of it passed over between 236° and 238°, but showed no signs of crystallising after standing in contact with a crystal of the *trans*-acid at  $-10^{\circ}$  for half an hour. In order to determine whether any change had taken place, the acid was converted into the acid chloride by treating it with the calculated quantity of phosphorus pentachloride, and the oxychloride removed by passing a current of dry air through the mixture heated at 100° under 50 mm. pressure. The oily residue was then poured into pure aniline, and after the excess of the latter had been removed by



shaking the ethereal solution of the product with dilute hydrochloric acid, it was dried over calcium chloride, and evaporated, and the anilide, which, on standing, became nearly solid, was spread on a porous plate and allowed to remain until free from oily mother liquor. As the nearly colourless residue had no definite melting point, it was ground up and extracted repeatedly with small quantities of cold ether; in this way a crystalline product was obtained which melted at 143—145°, and showed all the properties of the anilide of *trans*-hexahydro-orthotoluic acid, melting at 148°.

When this anilide was heated with hydrochloric acid in a sealed tube at 180° for one hour, the contents of the tube extracted with pure ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, an oily acid was left; this after being freed from ether by passing a current of dry air over it, was distilled and cooled to 0°, when it solidified almost completely. The crystalline mass, left in contact with porous porcelain until free from oil, melted at 41—44°, and after remelting and pressing between blotting paper, the melting point rose to 47—49°; the melting point of *trans*-hexahydro-orthotoluic acid being 50—52°. There can, therefore, be no doubt that during the treatment described above, the liquid *cis*-hexahydroorthotoluic acid had been converted into the stereoisomeric *trans*-modification.

The pure *trans*-acid was treated in exactly the same way as described above in the case of the *cis*-acid, when the product did not solidify until distilled, and even then not completely, as the crystals contained small quantities of an oily impurity readily removed by contact with porous porcelain; possibly this oily substance, which was present only in very small quantity, is the *cis*-acid, but this could not be satisfactorily proved, owing to lack of material.

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Manchester.*

SYNTHESIS OF INDENE, HYDRINDENE, AND  
SOME OF THEIR DERIVATIVES.

BY

W. H. PERKIN, JUN., PH.D., F.R.S.,

AND

G. RÉVAY, PH.D.

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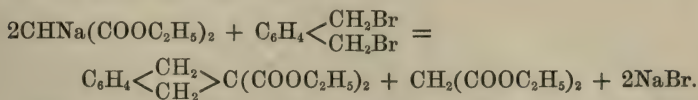
[From the Transactions of the Chemical Society, 1894.]



## Synthesis of indene, hydrindene, and some of their derivatives.

By W. H. PERKIN, Jun., Ph.D., F.R.S., and G. RÉVAY, Ph.D.

SOME time since (*Ber.*, **17**, 125; compare *Trans.*, 1888, **53**, 1), it was shown by v. Baeyer and one of us that ortho-xylylene dibromide and ethylic sodiomalonate react readily, forming sodium bromide and ethylic hydrindenedicarboxylate,\*

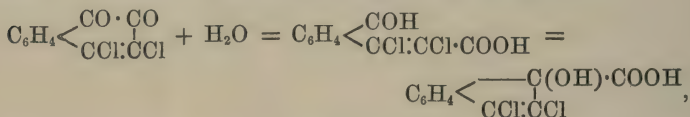


Hydrindenedicarboxylic acid is readily obtained from this ethereal salt on hydrolysis, and, when heated at 200°, the acid loses 1 mol. CO<sub>2</sub>, being converted into hydrindenecarboxylic acid.

\* Formerly called ethylic hydrindonaphtenecarboxylate.

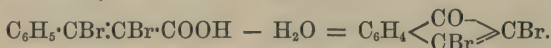


No further derivatives of hydrindene,  $C_6H_4<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH_2$ , or of the corresponding unsaturated hydrocarbon, indene,  $C_6H_4<\begin{smallmatrix} CH \\ CH_2 \end{smallmatrix}>CH$ , were obtained until the year 1886, when Zincke and his pupils showed that naphthaquinone derivatives might be converted into indene derivatives. Dichloro- $\beta$ -naphthaquinone, for example, is converted by alkalis into indenedichlorohydroxycarboxylic acid,



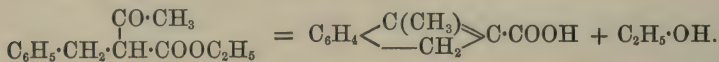
and this acid, when oxidised with chromic acid, yields  $\alpha$ -ketodichlorindene,  $C_6H_4<\begin{smallmatrix} CO \\ CCl \end{smallmatrix}>CCl$ .

Similarly constituted indene derivatives were subsequently obtained by Roser (*Ber.*, 1887, **20**, 1273) from dibromocinnamic acid by means of sulphuric acid,



These two syntheses were the first which yielded derivatives of indene; and the former is especially remarkable as illustrating the possibility of converting a 6-carbon ring into a 5-carbon ring, the naphthalene derivative being converted into an indene derivative; this curious change takes place apparently with the greatest readiness in the case of derivatives of  $\beta$ -naphthaquinone.

At a later date, Roser\* (*Annalen*, **247**, 157) studied the action of sulphuric acid on ethylic benzylacetoacetate, and showed that indene derivatives were formed thus,

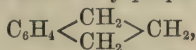


The carboxylic acid thus obtained, which Roser named  $\gamma$ -methylindene- $\beta$ -carboxylic acid, when heated alone, or, better, with soda-lime, yields  $\gamma$ -methylindene,  $C_6H_4<\begin{smallmatrix} C(CH_3) \\ \text{---}CH_2 \end{smallmatrix}>CH$ , the first hydrocarbon of the indene series which had been prepared. Subsequently several other general methods were discovered, by which a great variety of indene and hydrindene derivatives could be synthetically obtained; but it would take up too much space to mention these here.

Krämer and Spilker (*Ber.*, **17**, 125), in the course of a series of

\* Compare v. Pechmann (*Ber.*, **16**, 516).

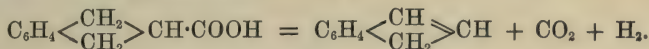
very interesting researches on some coal-tar products, succeeded in isolating from the fraction of coal tar, boiling at 176—182°, a hydrocarbon,  $C_9H_8$ , which on oxidation yielded phthalic acid, and which was evidently indene,  $C_6H_4<\begin{smallmatrix} CH \\ CH_2 \end{smallmatrix}>CH$ ; by reducing this hydrocarbon with sodium and alcohol they prepared hydrindene,



a hydrocarbon, which they subsequently showed to be also contained in coal tar.

The hydrindene thus obtained is the parent substance of the hydrindenecarboxylic acid obtained from ortho-xylene, as explained above; and, as we were engaged in a detailed investigation of this acid, it occurred to us that it would be interesting to endeavour to prepare a hydrocarbon from the acid, and then to compare it with the hydrindene obtained from coal tar.

The acid was decomposed in two ways, namely, by heating the barium salt alone, and by heating a mixture of the barium salt with sodium methoxide (compare Mai, *Ber.*, **22**, 2133); in both cases we obtained a considerable quantity of hydrocarbon, which, however, proved to be indene, and not hydrindene, the decomposition of the acid evidently taking place thus,



The hydrocarbon, thus synthetically prepared, yielded hydrindene on reduction; and both these hydrocarbons showed the closest resemblance to the substances of similar composition, isolated from coal tar by Krämer and Spilker.

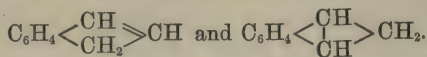
A careful examination of the physical properties of the indene from coal tar, and of synthetical indene, gave results which show, as we believe, that the two substances are not identical, although they have the same boiling point and show exactly the same chemical behaviour.

Indene from coal tar has a sp. gr.  $d_{40}^{40} = 1.0539$ , and the magnetic rotation  $15.100$ ;\*, the sp. gr. of synthetical indene, determined under similar conditions, was  $1.0059$ , and the magnetic rotation  $16.200$ .

Unfortunately, the various samples of coal tar indene which Dr. Spilker kindly sent us did not give very constant results on examination; but in all cases the density was much greater, and the magnetic rotation much less, than the values found in the case of synthetical indene.

\* These numbers are the average of the results obtained with two distinct samples.

Apparently, then, the two substances are not identical, and, theoretically, it is quite possible that two isomeric hydrocarbons,  $C_9H_8$ , can exist which may be very closely allied in properties; their constitutions would be represented by the formulæ



Such hydrocarbons would very probably differ but slightly in chemical properties, and, on reduction, they would probably yield one and the same hydrindene.

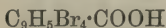
In order to determine whether the products of reduction were identical, hydrindene from coal tar indene was carefully compared with the substance obtained by the reduction of synthetical indene, and the result of the comparison may be summarised as follows.

	B. p.	Sp. gr. 4°/4°.	Mag. rot.
Hydrindene (coal tar)....	176·5—177·5°	0·9655	13·971
Hydrindene (synthetical).	176·0—176·5°	0·9732	13·904

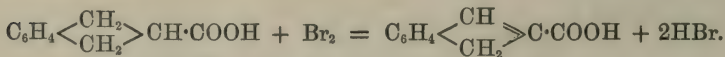
Although the results do not agree quite so closely as could have been desired, they nevertheless clearly indicate that the substances are identical; this is interesting when taken in connection with the fact that the unsaturated hydrocarbons from which they were derived are widely different in properties.

During the investigation of hydrindenecarboxylic acid, several new derivatives of this acid were prepared, and are described in detail in the paper; a brief summary of some of the more important results may be appended here.

When exposed to bromine vapour, hydrindenecarboxylic acid is converted quantitatively into *tetrabromhydrindenecarboxylic acid*,



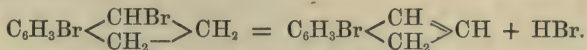
(m. p. 248—250°); but when a solution of the acid in chloroform is heated with bromine at 100° the action proceeds differently, 2 atoms of hydrogen are eliminated, and indenecarboxylic acid (m. p. 230°) is formed, thus—



As it seemed possible that all hydrindene derivatives might be oxidised to indene derivatives by similar treatment, we studied the action of bromine on hydrindene itself; but although apparently small quantities of indene are produced, the primary product appears to be a dibromhydrindene,  $C_6H_3Br \begin{smallmatrix} <CHBr \\ >CH_2 \end{smallmatrix} > CH_2$  (?), in which one of the bromine atoms is situated in the benzene ring, as is shown by

the fact that, when oxidised with nitric acid, bromophthalic acid is formed.

Dibromhydrindene may be distilled under diminished pressure, but at the ordinary pressure it is decomposed into bromindene and hydrogen bromide.



Hydrindenecarboxylic acid, when treated with phosphorous pentachloride, yields a well characterised crystalline acid chloride, which has been used in the synthesis of a number of derivatives of hydrindene described in this paper.

*Preparation of Hydrindenedicarboxylic acid,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{C}(\text{COOH})_2$ .*

A method of preparing this acid and the corresponding hydrindenemonocarboxylic has already been described by v. Baeyer and Perkin (*Ber.*, **17**, 122). Although this method answers very well for preparing the acids in small quantities, yet where large quantities are required, as was the case in carrying out the experiments described in this paper, it was found advantageous to introduce several modifications, more especially in the preparation and purification of the monocarboxylic acid.

We give in full the method which was ultimately adopted. In order, in the first place, to prepare the ethereal salt of hydrindenedicarboxylic acid, 6.3 grams of sodium is dissolved in 70 grams of pure absolute alcohol; the solution of sodium ethylate thus obtained, while still warm, is mixed with 250 c.c. of absolute ether (repeatedly distilled over sodium), 21 grams of ethylic malonate is added, and the mixture well shaken, and then a solution of 35 grams of ortho-xylylene dibromide in 250 c.c. of absolute ether is poured in. The clear solution soon begins to deposit sodium bromide, and, as the action proceeds, sufficient heat is generated to keep the liquid in a state of vigorous ebullition, so that it is necessary to connect the flask containing the mixture with a reflux apparatus. At the end of about three hours, the clear ethereal solution is decanted from the white precipitate, the ether distilled off, the residual oil again mixed with the white precipitate, and the whole hydrolysed by digestion with a solution of 20 grams of potassium hydrate in methylic alcohol for about 30 minutes, until a sample when dissolved in water produces only a slight milkiness. After distilling off the bulk of the methylic alcohol on a water-bath, the residue, which often has a peculiar violet colour, is dissolved in water and evaporated on a water bath till free from alcohol; the well-cooled solution is then extracted several times with ether in order to remove oily impurities. On acidifying the alkaline



solution, a brownish, crystalline precipitate of impure hydrindenedicarboxylic acid separates; this is dissolved in ether, the ethereal solution evaporated, and the residual brownish, crystalline mass purified by recrystallisation from water. In carrying out this operation, it is best to dissolve the crude acid in a large bulk of water at about  $90^{\circ}$ , filter from undissolved dark coloured impurities, and then concentrate slowly on a water bath. During the concentration, the bibasic acid separates in crystalline crusts, the quantity of which increases largely as the liquid cools; these crusts, when recrystallised from water, yield beautiful, colourless crystals which consist of pure hydrindenedicarboxylic acid, as the following analysis shows.

0.1606 gave 0.3762  $\text{CO}_2$  and 0.0724  $\text{H}_2\text{O}$ .  $\text{C} = 63.88$ ;  $\text{H} = 5.01$ .

$\text{C}_{11}\text{H}_{10}\text{O}_4$  requires  $\text{C} = 64.07$ ;  $\text{H} = 4.86$  per cent.

Hydrindenedicarboxylic acid melts at  $199^{\circ}$ , as stated in the first paper on this subject.

*Hydrindenemonocarboxylic acid*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CH}\cdot\text{COOH}$ .

This acid may be readily obtained in small quantities in a pure state by the method first described by Baeyer and Perkin, namely, by the distillation of the bibasic acid; but, in preparing large quantities, a much better yield of pure substance is obtained by the following process. The crude, brownish, bibasic acid obtained by hydrolysing the product of the action of ortho-xylylene dibromide on ethylic sodiomalonate, and extracting with ether, as described above, is heated at  $200^{\circ}$  in an oil bath until the evolution of carbonic anhydride has entirely ceased. The dark-coloured product is then dissolved in a hot dilute solution of sodium carbonate, filtered from undissolved impurities, and reprecipitated with hydrochloric acid, care being taken that the acid does not cake together. The precipitate, after being collected and well washed with water, is ground up with water in a mortar to a fine paste, and gradually added to a slight excess of a hot dilute solution of barium hydrate. The greater part of the acid dissolves, forming a colourless solution, whereas the dark-coloured impurities cake together, forming resinous lumps, which, however, still contain some of the acid; the recovery of this is described below. After filtration, the alkaline solution of the barium salt is acidified with hydrochloric acid, and the colourless, crystalline precipitate collected, washed with water, and dried at  $100^{\circ}$ ; it is almost pure hydrindenecarboxylic acid, and was the material used in the following experiments. An analysis was made of the acid recrystallised from water.

0.1478 gave 0.4004  $\text{CO}_2$  and 0.0838  $\text{H}_2\text{O}$ .  $\text{C} = 73.90$ ;  $\text{H} = 6.30$ .

$\text{C}_{10}\text{H}_{10}\text{O}_2$  requires  $\text{C} = 74.07$ ;  $\text{H} = 6.17$  per cent.

The yield of hydrindenecarboxylic acid obtained in this way is good (about 70 per cent. of the theoretical), but considerable quantities are retained in the brown lumps mentioned above. The purification of this uninviting product is a matter of some difficulty, but it may be accomplished by converting the acid into its methylic salt, which, after fractional distillation, yields the pure acid on hydrolysis.

To this end, the brown resinous mass is boiled with dilute potassium hydrate solution, filtered, and the crude acid reprecipitated and washed well with water. The almost black product is dried at 100°, dissolved in 10 times its weight of methylic alcohol, saturated with gaseous hydrogen chloride without cooling, and, after standing for two days, the liquid is poured into ice-cold water. The methylic salt is extracted with ether, the ethereal solution well washed, first with water and subsequently with sodium carbonate solution, and dried over anhydrous potassium carbonate; the ether is then distilled off, and the residue submitted to fractional distillation under reduced pressure. The almost colourless oil which distils between 160° and 185° (80 mm.) is hydrolysed by boiling with alcoholic potash, the potassium salt freed from alcohol by evaporation, dissolved in water, acidified with hydrochloric acid, and the resulting almost colourless acid purified by recrystallisation from water or from acetic acid.

It may here be mentioned that a cold solution of hydrindenecarboxylic acid in dilute sodium carbonate solution does not decolorise potassium permanganate except on standing.

*Barium hydrindenecarboxylate*.—Quantities of this salt were obtained during the purification of the acid as described above. It is readily soluble in water, and crystallises from a concentrated solution in colourless needles which contain water of crystallisation.\*

I. 0.2660 gave 0.1353 BaSO<sub>4</sub>. Ba = 29.86 per cent.

II. 0.2688 „ 0.1365 „ Ba = 29.87 „

C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>Ba requires Ba = 29.84 per cent.

*Methylic Hydrindenecarboxylate*, C<sub>6</sub>H<sub>4</sub>< $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$ >CH·COOCH<sub>3</sub>.

This ethereal salt was obtained in considerable quantities in the purification of crude hydrindenecarboxylic acid (see above), but as this crude product is difficult to purify, a small quantity of the methylic salt was prepared from the pure acid in the following manner: 10 grams of pure dry hydrindenecarboxylic acid was dissolved in 50 grams of methylic alcohol, the solution saturated, without cooling, with

\* The numbers obtained in the estimation of the amount of water of crystallisation have unfortunately been lost.

dry hydrogen chloride, allowed to stand for two days, and then warmed on a water bath in a reflux apparatus for about half an hour. The well-cooled product was poured into ice-cold water, the methylic salt extracted with ether, and the ethereal solution washed well, first with water, then with sodium carbonate solution; it was then dried over anhydrous potassium carbonate, evaporated, and the brownish oily residue purified by fractionation under reduced pressure.

Methylic hydrindenecarboxylate boils at  $170^{\circ}$  under a pressure of 60 mm., and the colourless distillate, on standing for a long time, solidifies to a mass of colourless crystals which melt at a low temperature.

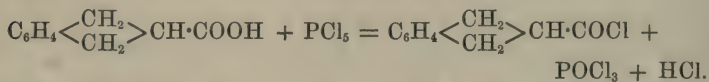
0.1450 gave 0.3981  $\text{CO}_2$  and 0.0907  $\text{H}_2\text{O}$ .  $\text{C} = 74.87$ ;  $\text{H} = 6.95$ .

$\text{C}_{11}\text{H}_{12}\text{O}_2$  requires  $\text{C} = 75.00$ ;  $\text{H} = 6.82$  per cent.

Methylic hydrindenecarboxylate, when pure, distils under the ordinary pressure with only slight decomposition. It has a peculiar faintly aromatic smell, and is insoluble in water; when boiled with alcoholic potash, it is readily hydrolysed.

*Hydrindenecarboxylic Chloride*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CH}\cdot\text{COCl}$ .

This is readily obtained by the action of phosphorous pentachloride on hydrindenecarboxylic acid, according to the equation



In preparing this substance it is important to operate as quickly as possible, and prolonged heating of the product should be especially avoided, as otherwise the whole mass is apt to be decomposed. The following method may be advantageously employed in preparing considerable quantities of this chloride. 25 grams of pure phosphorus pentachloride are introduced into a distillation flask, which must be of such a capacity as to allow of the subsequent convenient distillation of the product under diminished pressure; and then 16 grams of pure dry hydrindenecarboxylic acid in the form of lumps (not of powder, as the reaction may easily become very violent) is added all at once. In a short time a vigorous action sets in with evolution of torrents of hydrogen chloride, and ultimately the whole mass liquefies. As soon as the action has completely subsided the flask is connected with an apparatus for distillation under diminished pressure (100 mm.), and the product rapidly fractionated.

After the phosphorous oxychloride has passed over, the thermometer rises rapidly to  $178^{\circ}$ , between which temperature and  $182^{\circ}$  the



acid chloride distils. An analysis of this product was made by Carius' method.

0.2554 gave 0.2014 AgCl.  $\text{Cl} = 19.51$ .

$\text{C}_{10}\text{H}_9\text{ClO}$  requires  $\text{Cl} = 19.69$  per cent.

When freshly distilled, hydrindenecarboxylic chloride is a colourless, pungent-smelling oil, which, although it may sometimes remain liquid for days, generally solidifies rapidly to a mass of colourless prisms; it melts at approximately  $35\text{--}38^\circ$ ; and, when pure, boils constantly at  $180^\circ$  (100 mm.). It is moderately readily decomposed by cold water and by alcohol, very readily when warmed with these liquids.

*Amide of Hydrindenecarboxylic acid*,  $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle\text{CH}\cdot\text{CONH}_2$ .

This was prepared in two different ways, namely (I) by the action of ammonium carbonate on hydrindenecarboxylic chloride, and (II) by the action of ammonia on methylic hydrindenecarboxylate.

*Method I.*—Pure hydrindenecarboxylic chloride was ground up in a mortar with excess of ammonium carbonate until all action had ceased; the mixture, after three hours, was treated with water, and the crude insoluble amide collected and washed well, first with dilute sodium carbonate solution, and subsequently with water. It was then dried on a porous plate, and recrystallised from methylic alcohol.

*Method II.*—Pure methylic hydrindenecarboxylate, 10 grams, was heated in a sealed tube with 30 c.c. of strongest aqueous ammonia solution for three hours at  $120^\circ$ ; the tube was then opened, the contents again saturated with ammonia, and the heating at  $120^\circ$  continued for three hours more. The tube, on cooling, was found to be filled with hard lumps interspersed with beautiful, glistening plates. The solid substance was collected, washed with water, dried on a porous plate, and recrystallised three times from methylic alcohol. In this way, magnificent, colourless prisms were obtained, which, on analysis, gave the following numbers.

0.1324 gave 10.4 c.c. moist nitrogen at  $23^\circ$  and 752 mm.  $\text{N} = 8.75$ .

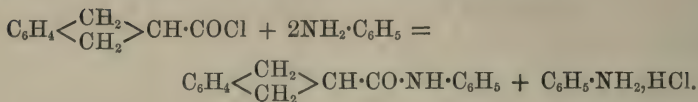
$\text{C}_{10}\text{H}_{11}\text{NO}$  requires  $\text{N} = 8.69$  per cent.

The amide of hydrindenecarboxylic acid melts at  $178^\circ$ ; it is readily soluble in alcohol, sparingly in chloroform, and almost insoluble in water. When rapidly heated, small quantities distil apparently without decomposition.

*Anilide of Hydrindenecarboxylic acid*,  $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ .

This substance is readily produced by the interaction of hydrindenecarboxylic chloride and aniline thus,





Freshly distilled aniline in excess is added to pure hydrindenecarboxylic chloride, and the mixture, as soon as the somewhat violent action which sets in has subsided, heated for almost half an hour on a water bath. In order to purify the crude solid product, it is ground up with very dilute hydrochloric acid, well washed with water, dried on a porous plate, and recrystallised once or twice from ethylic alcohol. The beautiful, glistening plates thus obtained gave the following results on analysis.

0.1520 gave 8.2 c.c. moist nitrogen at 19° and 758 mm. N = 6.18.

$\text{C}_{16}\text{H}_{15}\text{NO}$  requires N = 5.91 per cent.

The anilide of hydrindenecarboxylic acid melts at 182°; it is very sparingly soluble in cold alcohol, but dissolves more readily in the boiling solvent; the solution, on cooling, deposits the anilide in beautiful, glistening plates.

It is readily soluble in hot acetic acid, and crystallises beautifully from this solvent, in thin, four-sided plates; it dissolves sparingly in chloroform, and is almost insoluble in light petroleum.

*Action of Bromine Vapour on Hydrindenecarboxylic acid.*

Finely divided hydrindenecarboxylic acid is readily acted on when exposed under a bell jar to the vapour of bromine. A quantitative experiment showed that 4 atoms of bromine are taken up with formation of tetrabromhydrindenecarboxylic acid; 0.8610 gram of acid, exposed to the vapour of bromine for five days, and then allowed to stand in a vacuum desiccator over potash until the excess of bromine had evaporated, gained 1.647 grams. The calculated gain for the formation of an acid,  $\text{C}_{10}\text{H}_6\text{Br}_4\text{O}_2$ , is 1.67 grams. The bromo-acid is sparingly soluble in cold acetic acid, but dissolves more readily on boiling; the solution, on cooling, deposits the acid in colourless needles, which appear to contain acetic acid of crystallisation, as they become opaque on drying at 100°.

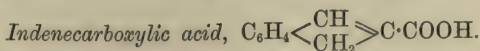
0.1648 gave 0.1520  $\text{CO}_2$  and 0.0211  $\text{H}_2\text{O}$ . C = 25.15; H = 1.41.

0.2963 „ 0.4630 AgBr; Br = 66.55.

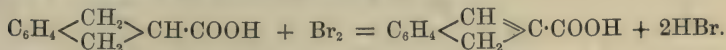
$\text{C}_{10}\text{H}_6\text{Br}_4\text{O}_2$  requires C = 25.10; H = 1.25; Br = 66.92 per cent.

Tetrabromhydrindenecarboxylic acid melts at 248–250°. It is sparingly soluble in methylic alcohol, chloroform, light petroleum, ether, and benzene; more readily in boiling toluene and xylene. The sodium salt is sparingly soluble in water, and separates, on dissolving the acid in soda, as a white, gelatinous mass. The cold dilute

solution of the acid in sodium carbonate does not decolorise permanganate.



When subjected to the action of bromine in chloroform solution, hydrindenecarboxylic acid is partly converted into indenecarboxylic acid, with loss of 2 atoms of hydrogen, thus :



The study of this interesting action is rendered difficult, as very slight variations in the conditions of the experiment give rise to the formation of very different products. In several instances where the conditions apparently were precisely similar, sometimes a very good yield of indenecarboxylic acid was obtained, whilst at other times the product was resinous, and very difficult to purify. In carrying out the experiment, 4.5 grams of hydrindenecarboxylic acid were dissolved in 20 c.c. of pure dry chloroform, 4.1 grams of dry bromine added, and the mixture heated in a water bath at  $100^\circ$  for about 1 hour. After standing over night, the tube was seen to contain a quantity of beautiful glistening plates; these were collected, washed with a little chloroform, spread on a porous plate, and recrystallised from dilute acetic acid and from chloroform, until the melting point was constant. The analysis gave results which agree with the formula of indenecarboxylic acid.

I. 0.1561 gave 0.4270  $\text{CO}_2$  and 0.0717  $\text{H}_2\text{O}$ . C = 74.60; H = 5.10.

II. 0.1734 „ 0.4752  $\text{CO}_2$  and 0.0790  $\text{H}_2\text{O}$ . C = 74.75; H = 5.06.

$\text{C}_{10}\text{H}_8\text{O}_2$  requires C = 75.00; H = 5.00 per cent.

The chloroform filtrate, which was separated from the crystals of indenecarboxylic acid, as described above, and which still contained the greater part of the substance, was well washed with water to remove hydrogen bromide, dried over calcium chloride, the bulk of the chloroform distilled off, and the residual concentrated solution allowed to stand for some days in a cold place. In this way a further crop of crystals of indenecarboxylic acid was obtained, but these were dark coloured and much more difficult to purify. Lastly, the mother liquor from these crystals, on evaporation, deposited an uninviting, reddish oil, which on long standing became pasty, owing to the separation of crystals, but these could not be separated from the resinous impurities by treatment with solvents. If, however, this crude product is distilled under diminished pressure, the oily distillate, on cooling, almost entirely solidifies, and on treating it with small quantities of chloroform to dissolve impurities a further quantity of indenecarboxylic acid may be obtained.

*Properties of Indenecarboxylic acid.*—Indenecarboxylic acid, when heated in a capillary tube, becomes soft at  $222^{\circ}$ , and melts not quite sharply at  $230^{\circ}$ . Small quantities of the pure acid, heated in a test tube, distil almost without decomposition, forming a wool-like sublimate in the cooler portions of the tube; on the hotter portions, an oil condenses which solidifies on cooling. The melting point of the distillate and the sublimate is about  $220^{\circ}$ , or a few degrees lower than that of the recrystallised acid. When carefully heated in a stream of an indifferent gas in a piece of combustion tube, indenecarboxylic acid sublimes in magnificent, iridescent needles, somewhat resembling a sublimate of benzoic acid.

Indenecarboxylic acid is readily soluble in alcohol, ether, acetic acid, and ethyl acetate, but only sparingly in chloroform, benzene, carbon bisulphide, or water, and almost insoluble in light petroleum. It crystallises from boiling water in colourless, microscopic needles; but it is most readily purified by recrystallisation from chloroform or dilute acetic acid.

A number of experiments were instituted with the object of obtaining a dibromindenecarboxylic acid,  $C_6H_4<\begin{smallmatrix} CHBr \\ CH_2- \end{smallmatrix}>CBr\cdot COOH$ , but without success. When dry indenecarboxylic acid is exposed to the action of bromine vapour it absorbs large quantities of the halogen, and is converted into a brownish mass, which is for the most part insoluble in alkaline carbonates, and which appears to contain dibromhydrindene,  $C_6H_4<\begin{smallmatrix} CHBr \\ CH_2- \end{smallmatrix}>CHBr$ . This substance is very difficult to purify, and no satisfactory analytical numbers could be obtained with the small quantity at our disposal.

Indenecarboxylic acid dissolves in concentrated sulphuric acid in the cold, forming a colourless solution, which on warming becomes brownish, but no resinous substance is formed in the cold, as is the case when indene itself is treated with sulphuric acid at the ordinary temperature. A solution of indenecarboxylic acid in cold, dilute sodium carbonate decolorises potassium permanganate instantly, as was to be expected, owing to its unsaturated nature and similarity in constitution to the tetrahydrophthalic acids.

*Salts of Indenecarboxylic acid. Silver salt,  $C_{10}H_7O_2Ag$ .*—This was prepared by precipitating a neutral solution of the ammonium salt with silver nitrate. It is an amorphous, white precipitate, which, on standing, acquires a glistening appearance, and thus apparently becomes crystalline.

0.2230 gave 0.0899 Ag.  $Ag = 40.31$ .

$C_{10}H_7O_2Ag$  requires  $Ag = 40.45$  per cent.

A dilute solution of the ammonium salt of indenecarboxylic acid

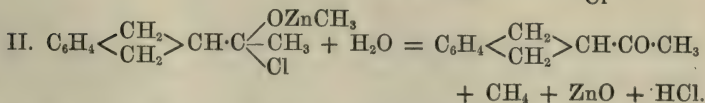
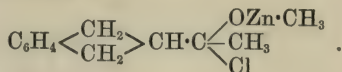
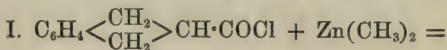


shows the following behaviour with reagents. *Copper acetate*, a heavy, light blue precipitate, insoluble in water. *Barium chloride*, a white, crystalline precipitate gradually forms, which is moderately soluble in hot water. *Lead acetate*, a white, amorphous precipitate, which on boiling becomes caseous. *Calcium chloride*, a white, apparently crystalline precipitate, which is much less soluble than the barium salt. *Zinc chloride* and *cadmium chloride*, white precipitates; the cadmium salt becomes crystalline on boiling.

In preparing indenecarboxylic acid by the method described above, it happened, on several occasions, that no crystals separated from the chloroform solution of the product of the action of bromine on hydrindenecarboxylic acid, and, on evaporation, a semi-solid residue was left, containing apparently much unchanged substance, and from which no definite product could be obtained by treatment with solvents. From such a product, indenecarboxylic acid may be isolated in the following way. The crude substance is boiled with a considerable quantity of water, and milk of lime added, any slight excess being removed by passing a stream of carbonic anhydride through the boiling liquid. On concentrating the filtrate, and allowing it to stand, a calcium salt is deposited in curious nodules. The addition of hydrochloric acid to the aqueous solution of this salt precipitates a slightly coloured crystalline acid, which has no definite melting point. This is again converted into the calcium salt, and the treatment repeated until a colourless acid is obtained, which, after washing with small quantities of chloroform, melts above 200°; pure indenecarboxylic acid may be obtained from this by recrystallising from 80 per cent. acetic acid.

*Hydrindene Methyl Ketone*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{CO}\cdot\text{CH}_3$ .

The chloride of hydrindenecarboxylic acid and zinc methide interact in ethereal solution, forming a soluble zinc compound, which is decomposed by water, yielding hydrindene methyl ketone. This decomposition is probably represented thus:—



In preparing the zinc methide necessary for these experiments, the zinc-copper couple was, as recommended by Gladstone and Tribe



(Trans., 1879, **35**, 569), heated with methylic iodide under an extra pressure of about 500 mm. of mercury until the action was complete, and the zinc methiodide distilled directly into a weighed flask. In each case about 25 grams of zinc methide was prepared, and this was diluted with 100 c.c. of absolute ether, about 12 grams of hydrindenecarboxylic chloride added, and the mixture heated in a reflux apparatus for two days. The action does not take place readily as is the case when zinc ethide is used (see p. 243), and even after boiling for two days an appreciable amount of hydrindenecarboxylic chloride remains unacted on in spite of the large excess of zinc methide employed. In order to isolate the product, water was added very slowly and drop by drop from a dropping funnel, great care being necessary at this stage owing to the almost explosive violence of the action, and it is well, during the operation, to keep the flask containing the ethereal solution well cooled with ice-cold water. As soon as the decomposition of the zinc compound is complete, hydrochloric acid is added to dissolve the precipitated zinc hydroxide, and the whole extracted three times with ether.

The ethereal solution which contains, besides the hydrindene methyl ketone, considerable quantities of hydrindenecarboxylic acid (from undecomposed chloride), is repeatedly extracted with dilute potassium hydrate solution, dried over anhydrous potassium carbonate, and evaporated, the residual, almost colourless ketone being purified by fractionation under reduced pressure. Almost the whole passes over at 170—180° (80 mm.) at the first distillation, and on redistillation an oil is obtained which boils constantly at 175—177° (80 mm.).

0.1892 gave 0.5692 CO<sub>2</sub> and 0.1272 H<sub>2</sub>O. C = 82.05; H = 7.47.

C<sub>11</sub>H<sub>12</sub>O requires C = 82.50; H = 7.50 per cent.

Hydrindene methyl ketone is a colourless oil of feeble odour, and, in small quantities, may be distilled under the ordinary pressure with only very slight decomposition. The yield obtained in the above synthesis was comparatively small, owing to the fact that the product invariably contained unchanged acid chloride, from which, however, hydrindenecarboxylic acid may, of course, be again regenerated.

*Hydrindene Methyl Ketoxime*, C<sub>6</sub>H<sub>4</sub>< $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}$ >CH·C(CH<sub>3</sub>):NOH.

When treated with hydroxylamine in strongly alkaline solution, hydrindene methyl ketone is converted into a beautifully crystalline oxime, which serves as a valuable means of characterising the oily ketone.

In preparing this oxime, hydrindene methyl ketone (1.6 grams) was dissolved in a little alcohol, the solution mixed with a saturated

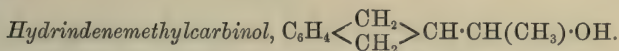
aqueous solution of hydroxylamine hydrochloride (1 gram), a moderately concentrated solution of alcoholic potash (containing 2 grams KOH) added, and the whole left for 24 hours. The product was then evaporated gently on a water bath till free from alcohol, diluted with water, and rendered slightly acid by the addition of dilute hydrochloric acid. The oxime, which was precipitated as a colourless solid, was collected, washed with water, and purified by recrystallisation from methylic alcohol. For analysis, it was dried at 100°.

0.1434 gave 0.3966 CO<sub>2</sub> and 0.0988 H<sub>2</sub>O. C = 75.42; H = 7.65.

0.2184 „ 16.4 c.c. moist nitrogen at 22° and 740 mm. N = 8.20.

C<sub>11</sub>H<sub>13</sub>NO requires C = 75.42; H = 7.43; N = 8.00 per cent.

Hydrindene methyl ketoxime melts at 125–126°. It is readily soluble in methylic alcohol, chloroform, benzene, and acetic acid, sparingly in light petroleum, and almost insoluble in water. It crystallises from methylic alcohol in magnificent glistening prisms, and from dilute acetic acid in needles. Hydrindene methyl ketoxime dissolves readily in concentrated hydrochloric acid on warming, and remains dissolved on diluting with water, but is reprecipitated on the addition of sodium carbonate; it dissolves, also, on warming with strong caustic potash solution, but if the solution is diluted and allowed to stand the oxime gradually separates in stellar groups of needles.

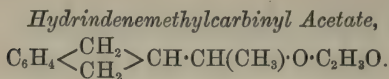


In reducing ketones which have a high molecular weight, as is the case with hydrindene methyl ketone, and which are almost insoluble in dilute alcohol, the best reagent for effecting this purpose is sodium in the presence of alcohol. The pure ketone was dissolved in alcohol and treated with twice the calculated quantity of sodium in a large flask connected with a reflux apparatus, the action being allowed to proceed as vigorously as possible. The product was mixed with water, extracted three times with ether, the ethereal solution washed well with water, dried over anhydrous potassium carbonate, evaporated, and the colourless oil thus obtained purified by distillation under reduced pressure. The fraction 185–190° (80 mm.), on standing, almost entirely solidified in the form of long, slender, striated needles; these were freed from oily mother liquor by spreading on a porous plate, dried over sulphuric acid, and analysed.

0.1357 gave 0.4051 CO<sub>2</sub> and 0.1055 H<sub>2</sub>O. C = 81.41; H = 8.64.

C<sub>11</sub>H<sub>14</sub>O requires C = 81.48; H = 8.65 per cent.

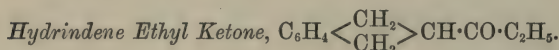
Hydrindenemethylcarbinol melts at about 48°, and has a peculiar, somewhat penetrating smell. It dissolves freely in most organic solvents.



In order to prepare this acetate, the pure carbinol was digested for two hours with excess of acetic anhydride, the anhydride distilled off, and the crude oily residue purified by fractionation under reduced pressure. Hydrindenemethylcarbinyl acetate is a colourless oil which boils at 188—190° (70 mm.) and has a peculiar odour, somewhat recalling that of toluene.

0.1425 gave 0.3982 CO<sub>2</sub> and 0.1020 H<sub>2</sub>O. C = 76.21; H = 7.94.

C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> requires C = 76.47; H = 7.84 per cent.



This interesting substance is much more easily prepared than the methyl ketone, and is obtained in very good yield by the action of zinc ethide on hydrindenecarboxylic chloride. The following are the details of the method of preparation employed. A flask of about 1½ litres capacity, containing about 70 c.c. of absolute ether (which had been freed from the last traces of alcohol and water by repeated distillation over sodium) was filled with dry carbonic anhydride, 10 grams of zinc ethide was added, and 17 grams of freshly distilled hydrindenecarboxylic chloride poured in. The mixture soon became warm, and, on standing for some time, the temperature gradually rose until the ether began to boil vigorously, so that it was necessary to moderate the action by cooling when it became too violent.

After the product had stood for about half an hour, 10 grams more of zinc ethide was added and the mixture heated to boiling for two hours in a reflux apparatus. The product was then decomposed by the careful addition of small quantities of water, the precipitated zinc hydroxide dissolved in dilute hydrochloric acid, and the ketone extracted by shaking three times with ether; the ethereal solution, after washing with water, was dried over anhydrous potassium carbonate, and evaporated. The residual oil was then purified by fractionation under reduced pressure, when the whole (15 grams) passed over between 188° and 190° (80 mm.), at the first distillation, as a colourless oil; this, on cooling, solidified almost completely in magnificent, four-sided plates. The crystalline mass after being freed from traces of oil by spreading it on a porous plate, was analysed.

0.1953 gave 0.5910 CO<sub>2</sub> and 0.1457 H<sub>2</sub>O. C = 82.53; H = 8.28.

C<sub>12</sub>H<sub>14</sub>O requires C = 82.76; H = 8.05 per cent.

Hydrindene ethyl ketone is a colourless crystalline substance, which melts at about 28° and distils at 188—190° (80 mm.).



*Hydrindene ethyl ketoxime*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{C}(\text{C}_2\text{H}_5):\text{NOH}$ .

This beautiful substance was prepared by the action of hydroxylamine on the pure ketone in the presence of a large excess of potassium hydrate. The following quantities were employed.

Hydrindene ethyl ketone, 4 grams dissolved in 10 c.c. of methyl alcohol.

Potassium hydrate, 8 grams dissolved in 30 c.c. of methyl alcohol.

Hydroxylamine hydrochloride, 3.5 grams dissolved in the smallest possible quantity of water.

The mixed solutions, on standing for 15 hours, deposited beautiful crystals, and on adding water and acidifying, a heavy, white precipitate was thrown down, which was extracted twice with ether; the ethereal solution was washed with water, dried over calcium chloride, and the ether distilled off. The residual oil solidified almost at once, and the crystalline mass was readily obtained quite colourless by washing with small quantities of ether. For analysis, the substance was dried over sulphuric acid.

0.1566 gave 10.2 c.c. moist nitrogen at 22.5°, and 756 mm. N = 7.38.

$\text{C}_{12}\text{H}_{15}\text{NO}$  requires N = 7.40 per cent.

Hydrindene ethyl ketoxime melts at 104°; it is readily soluble in alcohol, ether, benzene, and hot light petroleum, but only sparingly in cold light petroleum, and in water. It crystallises from dilute methylic alcohol in magnificent, colourless needles.

*Hydrindeneethylcarbinol*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot\text{OH}$ .

The reduction of hydrindene ethyl ketone was carried out, as in the case of the methyl ketone, by means of sodium and alcohol. The ketone was dissolved in absolute alcohol, and treated as rapidly as possible with twice the calculated quantity of sodium, the product allowed to cool, diluted with water, and extracted three times with ether; the ethereal solution was then well washed, dried over anhydrous potassium carbonate, and evaporated. The oily residue distilled constantly at 192° under a pressure of 80 mm., passing over as a colourless oil, which, on standing, solidified to a mass of concentrically grouped needles.

0.1427 gave 0.4280  $\text{CO}_2$  and 0.1166  $\text{H}_2\text{O}$ . C = 81.80; H = 9.10.

$\text{C}_{12}\text{H}_{16}\text{O}$  requires C = 81.81; H = 9.09 per cent.

Hydrindeneethylcarbinol crystallises from dilute methylic alcohol in magnificent, colourless needles, and melts at 67°. It is readily soluble in alcohol, benzene, and light petroleum, separating from its



hot solution in the latter solvent, on cooling, in long, colourless needles.

*Hydrindeneethylcarbinyl Acetate*,  $C_6H_4<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH\cdot CH(C_2H_5)\cdot O\cdot C_2H_5O$ .

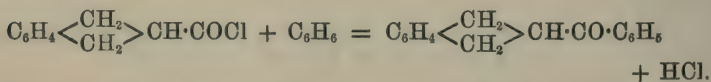
This acetate is readily prepared by digesting the pure carbinol with twice its weight of acetic anhydride for two hours, distilling off the excess of anhydride, and fractioning the residual oil under a pressure of 80 mm. It is a colourless oil boiling at  $210^\circ$  (80 mm.), and possessing an odour very similar to that of the corresponding hydrindenemethylcarbinyl acetate.

0.1713 gave 0.4820  $CO_2$  and 0.1310  $H_2O$ . C = 76.74; H = 8.49.

$C_{14}H_{18}O_2$  requires C = 77.06; H = 8.26 per cent.

*Hydrindene Phenyl Ketone*,  $C_6H_4<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH\cdot CO\cdot C_6H_5$ .

In the presence of aluminium chloride, hydrindenecarboxylic chloride and benzene readily interact, forming hydrindene phenyl ketone, thus:



In carrying out this synthesis, 25 grams of freshly distilled hydrindenecarboxylic chloride was dissolved in 100 grams of pure, dry benzene (free from thiophen) in a litre flask, and 30 grams of aluminium chloride added to it in small quantities at a time. As soon as the principal action, which rapidly sets in, had subsided, and the liquid cooled down again, the flask was connected with a reflux apparatus, and heated in a water bath for three hours. The dark coloured product was then poured into ice cold water, extracted several times with ether, and, after the ethereal solution had been well washed, first with water and then with dilute sodium carbonate solution, it was dried over calcium chloride, and the ether and benzene distilled off.

The brownish oily residue was then heated in a dish on a water bath until quite free from benzene, allowed to stand, and the dark yellow, crystalline cake which formed freed, as far as possible, from oily impurities by leaving it in contact with a porous plate for some days. The ochre coloured residue was then further purified by repeated recrystallisation from methylic alcohol.

0.1453 gave 0.4602  $CO_2$  and 0.0866  $H_2O$ . C = 86.38; H = 6.62.

$C_{16}H_{14}O$  requires C = 86.49; H = 6.30 per cent.

Hydrindene phenyl ketone melts at about  $107^\circ$ . It is readily soluble in hot alcohol, acetic acid, benzene, carbon bisulphide, and

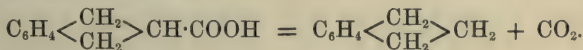
chloroform, less soluble in ether, sparingly soluble in cold methylic alcohol. It crystallises from methylic alcohol in almost colourless, fluffy masses consisting of microscopic needles; when heated in small quantities in a test tube, it distils with only slight decomposition. Experiments on the preparation of the oxime of this ketone were not attended with satisfactory results, as the oxime is not easily formed, and the product is also very difficult to purify. Reduction with sodium and alcohol converts the ketone into an uninviting resinous substance, from which small quantities only of a crystalline substance could be obtained.

*Preparation of Indene,  $C_6H_4<\begin{smallmatrix} CH \\ CH_2 \end{smallmatrix}>CH$ , from Hydrindenecarboxylic acid.*

In the course of their investigation of coal tar oil, Krämer and Spilker (*Ber.*, **23**, 3276) isolated from the fraction 176—182° an unsaturated hydrocarbon,  $C_9H_8$ , which they showed from its properties, and particularly from its behaviour on oxidation, to be indene,  $C_6H_4<\begin{smallmatrix} CH \\ CH_2 \end{smallmatrix}>CH$ , and this hydrocarbon, by treatment with sodium

and alcohol, was converted into hydrindene,  $C_6H_3<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH_2$ .

In the course of our experiments on hydrindene and indene derivatives, we have endeavoured to obtain the former hydrocarbon synthetically, that is, by the removal of carbon dioxide from hydrindenecarboxylic acid, thus,



and on experimenting on the action of heat on the barium salt of hydrindenecarboxylic acid, both alone and in the presence of sodium methoxide, we obtained considerable quantities of a hydrocarbon; this, however, proved to be indene and not hydrindene, loss of hydrogen having taken place during the decomposition. In carrying out these experiments, the first method employed was that recommended by Mai (*Ber.*, **22**, 2133) for the preparation of hydrocarbons of high molecular weight from their carboxylic acids, namely, distillation of a mixture of the barium salt of the acid with sodium methoxide under reduced pressure. Molecular proportions of pure, dry barium hydrindenecarboxylate and of sodium methoxide (dried at 200° in a stream of hydrogen) were intimately mixed in a hot mortar, and then transferred to a retort, which was connected with a water condenser and receiver, the latter being attached to a vacuum pump. On carefully heating the retort with a bunsen flame, the mixture soon began to decompose, with evolution of dense vapours

and distillation of a yellow oil, the contents of the retort becoming quite black and intumescing considerably, especially towards the close of the operation (which was conducted throughout under a pressure of 100 mm.).

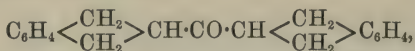
The oily distillate (from 28 grams of barium salt), about 10 grams, contained some drops of water; it was dissolved in ether, the ethereal solution dried over anhydrous potassium carbonate, evaporated, and the residual oil submitted to fractional distillation. During the first distillation, 7 grams passed over between 176° and 185° as a colourless oil, from which, on repeated fractionation over sodium, a comparatively large proportion was very easily obtained, boiling constantly at 180·5—181° (764 mm.). It gave the following numbers on analysis.

0·1570 gave 0·5354 CO<sub>2</sub> and 0·1005 H<sub>2</sub>O. C = 93·01; H = 7·11.

C<sub>9</sub>H<sub>8</sub> requires C = 93·10; H = 6·90 per cent.

The formula of this hydrocarbon was, therefore, C<sub>9</sub>H<sub>8</sub>, and a further study of its properties proved it to be indene, C<sub>6</sub>H<sub>4</sub>< $\begin{smallmatrix} \text{CH} \\ \text{CH}_2 \end{smallmatrix}\right\rangle\text{CH}$ , and apparently identical with the substance obtained by Krämer and Spilker from coal tar (b. p. 179·5—180·5° corr.). Thus the hydrocarbon obtained by us, when mixed with a drop of concentrated sulphuric acid, was converted into the peculiar, reddish-brown resin described by Krämer and Spilker, and called by them paraindene. When mixed with picric acid in benzene solution, a beautiful, brilliant, yellow picrate was obtained, very similar in properties to the picrate of the indene obtained from coal tar. Lastly, when reduced by sodium and alcohol, our hydrocarbon was converted quantitatively into a hydrocarbon, C<sub>9</sub>H<sub>10</sub>, identical with the hydrindene obtained by Krämer and Spilker under similar conditions from coal tar indene.

Some time after completing these experiments, and in the hope of obtaining dihydrindene ketone,

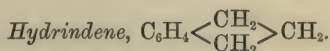


and hydrindene aldehyde, C<sub>6</sub>H<sub>4</sub>< $\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\right\rangle\text{CH}\cdot\text{COH}$ , we prepared the barium salt of hydrindenecarboxylic acid, and carefully studied the action of heat on the dry salt alone, and also on a mixture of the salt with barium formate. On distilling the barium salt alone, under reduced pressure (100 mm.), decomposition took place very readily, and a yellow oil passed over, which, after drying in ethereal solution over potassium carbonate and fractionation, yielded an oil boiling at 175—185°; a very small quantity of an oil of high boiling point was also obtained, but was not further examined. The fraction 175—185°,



when twice distilled over sodium, passed over almost entirely at 180—180·5°, and on examination and analysis was found to consist of pure indene. Found C = 92·91; H = 7·10 per cent. Theory for  $C_9H_8$ : C = 93·10; H = 6·90 per cent.

This result was the more remarkable in view of the fact that the hydrocarbon was produced in such large quantity, the amount actually obtained being only slightly below that from the distillation of a mixture of the barium salt with sodium methoxide. Similar results were obtained on distilling a mixture of the barium salt with barium formate. The oily distillate gave no trace of a compound with sodium hydrogen sulphite, showing that no aldehyde had been produced, and on fractionation an oil was obtained which had all the properties of indene.



The reduction of indene to hydrindene was carried out in the following way. Pure indene was dissolved in ethylic alcohol, and treated as rapidly as possible with three times the calculated quantity of sodium, and the product mixed with water; the milky liquid was then extracted three times with ether, the ethereal solution washed with water until free from alcohol, dried over anhydrous potassium carbonate, and evaporated. After fractioning the residual hydrocarbon three times over sodium, a colourless oil was obtained which boiled constantly at 176—177°.

0·1612 gave 0·5409  $CO_2$  and 0·1249  $H_2O$ . C = 91·51; H = 8·61.

$C_9H_{10}$  requires C = 91·53; H = 8·47 per cent.

This substance is identical with the hydrindene described by Krämer and Spilker (*loc. cit.*, p. 3281), which boils at 176—176·5° (corr.). It differs very markedly from indene in that it gives no resinous substance when treated with concentrated sulphuric acid, the hydrocarbon remaining apparently unchanged at ordinary temperatures; in fact Krämer and Spilker purified their hydrindene from indene by treatment with concentrated sulphuric acid and subsequent distillation in steam.

*Determination of the Density, Magnetic Rotation, and Refractive Power of Coal Tar and Synthetical Indene and Hydrindene.*

Although the boiling points and general chemical properties of the specimens of indene and hydrindene obtained from hydrindene-carboxylic acid agree well with those of the hydrocarbons isolated from coal tar by Krämer and Spilker, it was thought that before deciding as to the identity of the various products, it would be well if their physical properties were studied side by side; and we are



much indebted to Dr. Spilker for supplying us with several samples of his purest coal tar indene and hydrindene, thus enabling a direct comparison to be made.

The determination of the density, magnetic rotation, and refractive power of the following specimens was carried out by W. H. Perkin, Sen., and yielded very remarkable results, which appear to show that the indene from coal tar is not identical with that obtained from the barium salt of hydrindenecarboxylic acid, although the hydrindenes obtained from these substances on reduction appear to be identical.

I. Indene from barium hydrindenecarboxylate distilled twice over sodium. B. p. 181°.

*Density Determinations.*— $d\ 4^{\circ}/4^{\circ} = 1.0059$ ;  $d\ 10^{\circ}/10^{\circ} = 1.0008$ ;  $d\ 15^{\circ}/15^{\circ} = 0.9970$ ;  $d\ 20^{\circ}/20^{\circ} = 0.9934$ ;  $d\ 25^{\circ}/25^{\circ} = 0.9906$ .

*Magnetic Rotation.*

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.3°	2.5573	16.200

*Refractive Power.*

	A.	C.	D.	F.	G.	H.
$\mu$ ....	1.55680	1.57354	1.57980	1.59693	1.61219	—
$\frac{\mu - 1}{d}$ .	0.56551	0.57224	0.57849	0.59558	0.61080	—
$\frac{\mu - 1}{d}p$	65.599	66.380	67.105	69.086	70.853	72.573

II. Indene from coal tar.

Specimen (A) was distilled twice from sodium, which removed a quantity of a black substance. B. p. 179.5—180.5°.

*Density Determinations.*— $d\ 4^{\circ}/4^{\circ} = 1.0277$ ;  $d\ 10^{\circ}/10^{\circ} = 1.0225$ ;  $d\ 15^{\circ}/15^{\circ} = 1.0187$ ;  $d\ 20^{\circ}/20^{\circ} = 1.0152$ ;  $d\ 25^{\circ}/25^{\circ} = 1.0221$ .

*Magnetic Rotation.*

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.6°	2.4353	13.352

*Refractive Power.*

	A.	C.	D.	F.	G.	H.
$\mu$ ....	1.55818	1.56454	1.57107	1.58743	1.60220	—
$\frac{\mu - 1}{d}$ .	0.54726	0.55349	0.55990	0.57549	0.59042	—
$\frac{\mu - 1}{d}p$	63.482	64.205	64.948	66.809	68.489	—

The density of indene from the barium salt is lower, the magnetic rotation and refractive power considerably higher, than these values of coal tar indene.

Dr. Spilker suggested that these discrepancies might be due to the contamination of the coal tar indene with some hydrindene produced when the hydrocarbon, which was possibly not quite dry, was distilled over sodium; he then, very kindly, sent another sample (B), which was fractioned over caustic potash, and the portion boiling at 178—179° was examined.

*Density Determinations.*— $d\ 4^{\circ}/4^{\circ} = 1.06001$ ;  $d\ 15^{\circ}/15^{\circ} = 1.05086$ ;  $d\ 25^{\circ}/25^{\circ} = 1.04391$ .

*Magnetic Rotation.*

<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	2.4357	14.946

Both these series of numbers are higher than those first obtained with Sample A.

This sample was then purifieded by conversion into the picrate, according to Krämer and Spilker's directions; it was dehydrated by distilling over potash, and the fraction 178.5° to 179.5° examined.

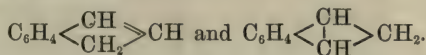
*Density Determinations.*— $d\ 4^{\circ}/4^{\circ} = 1.0479$ ;  $d\ 10^{\circ}/10^{\circ} = 1.0427$ ;  $d\ 15^{\circ}/15^{\circ} = 1.0387$ ;  $d\ 20^{\circ}/20^{\circ} = 1.0350$ ;  $d\ 25^{\circ}/25^{\circ} = 1.0319$ .

*Magnetic Rotation.*

<i>t.</i>	Sp. rotation.	Mol. rotation.
21.5°	2.4481	15.255

These numbers differ slightly from those obtained before conversion into the picrate, the density being lower and the magnetic rotation somewhat higher.

In comparing the results obtained in the examination of the indene prepared from the barium hydrindenecarboxylate with these last numbers, it will be noticed that the density of the former is much lower (0.0420 at 4°) than that of the latter, while the magnetic rotation is much higher (0.945). The differences are so large that they can scarcely be due to slight impurity, and it appears probable, therefore, that the two hydrocarbons are distinct, and represented possibly by the formulæ



It would, however, be very difficult to decide which of these represents coal tar indene for example.

*Hydrindene* (from hydrindenecarboxylic acid) prepared by reducing with sodium and alcohol the specimen of indene used in the determinations just described, was fractioned three times over sodium. B. p. 176.5—177.5°.

*Density Determinations.*— $d\ 4^{\circ}/4^{\circ} = 0.9732$ ;  $d\ 10^{\circ}/10^{\circ} = 0.9681$ ;  $d\ 15^{\circ}/15^{\circ} = 0.9645$ ;  $d\ 20^{\circ}/20^{\circ} = 0.9611$ ;  $d\ 25^{\circ}/25^{\circ} = 0.9559$ .

*Magnetic Rotation.*

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.25°	2.0399	13.904

*Refractive Power.*

	A.	C.	D.	F.	G.	H.
$\mu$ ....	1.52899	1.53394	1.53877	1.55114	1.56136	—
$\frac{\mu - 1}{d}$	0.54950	0.55474	0.55977	0.57261	0.58323	—
$\frac{\mu - 1}{d}p$	64.850	65.460	66.053	67.572	68.829	70.00

*Hydrindene* from coal tar, distilled three times over sodium. B. p. 176—176.5°.

*Density Determinations.*— $d$  4°/4° = 0.9655;  $d$  10°/10° = 0.9606;  $d$  15°/15° = 0.9570;  $d$  20°/20° = 0.9536;  $d$  25°/25° = 0.9507.

*Magnetic Rotation.*

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.95°	2.0465	13.971

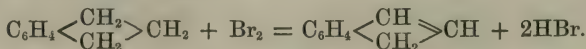
*Refractive Power.*

	A.	C.	D.	F.	G.
$\mu$ .....	1.52908	1.53431	1.53896	1.55105	1.56154
$\frac{\mu - 1}{d}$ ....	0.55123	0.55669	0.56153	0.57412	0.58506
$\frac{\mu - 1}{d}p$ ...	64.046	65.689	66.261	67.747	69.039

Although the two sets of numbers do not agree as well as could be desired, they are still sufficiently close to show that the two samples of hydrindene, obtained by such different methods, are in all probability identical, not only in chemical, but also in physical, properties.

*Action of Bromine on Hydrindene.*

When hydrindenecarboxylic acid is treated with bromine in chloroform solution, it is converted, in part at least, into indenecarboxylic acid, with loss of 2 atoms of hydrogen; and it appeared interesting to determine whether hydrindene itself under similar circumstances would yield indene. Thus,



11 grams of hydrindene was dissolved in 30 grams of pure dry chloroform, and 16 grams of bromine, dissolved in 10 grams of chloroform, added from a dropping funnel. Hydrogen bromide was evolved

in abundance, and the action was so energetic that it was necessary from time to time to cool the mixture. As soon as the action was finished, the product was dissolved in ether, washed well with water and dilute sodium carbonate solution, dried over calcium chloride, and the ether and chloroform distilled off. The residue was then divided into two parts, one of which (I) was distilled under reduced pressure, and the other (II) under ordinary pressures.

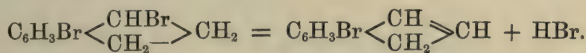
I. On fractioning the almost colourless oil under a pressure of 50 mm., a considerable portion distilled between 115° and 140°, and the temperature then rose rapidly to 175°, the greater portion distilling between 180° and 185°, a little hydrogen bromide being given off. The colourless product, which fumed only very slightly, gave on analysis numbers agreeing approximately with those required for dibromhydrindene.

0.1505 gave 0.2241 CO<sub>2</sub> and 0.0458 H<sub>2</sub>O. C = 40.61; H = 3.38.

0.2205 „ 0.2951 AgBr. Br = 56.97.

C<sub>9</sub>H<sub>5</sub>Br<sub>2</sub> requires C = 39.13; H = 2.90; Br = 57.97 per cent.

The dibromhydrindene thus produced has probably the constitution C<sub>6</sub>H<sub>3</sub>Br< $\begin{smallmatrix} \text{CHBr} \\ \text{CH}_2- \end{smallmatrix}$ >CH<sub>2</sub>. It is a colourless oil, which, when distilled under ordinary pressures, and also when repeatedly fractioned under reduced pressure, is decomposed into hydrogen bromide and monobromindene (see below).



The fraction 115—140° (50 mm.) which contained hydrogen bromide, was washed with water and carbonate of soda solution, and dried over calcium chloride; on distillation, the greater portion came over between 175° and 182°, consisting apparently of a mixture of much unchanged hydrindene with some indene. The presence of the latter is rendered probable by the fact that, on treatment with sulphuric acid, this fraction gave a yellowish-red amorphous substance, resembling indene resin in all respects.

II. The second portion of the crude product of the action of bromine on hydrindene was distilled under ordinary pressure, when a considerable quantity passed over below 200°; the temperature then rose rapidly to 230°, between which and 250° almost the whole distilled, abundance of hydrogen bromide being evolved during the operation. This fraction was dissolved in ether, washed with sodium carbonate, dried, the ether distilled off, and the oil submitted to repeated fractionation. In this way a colourless oil was obtained, boiling at 242—244°, and on analysis gave the following results.



0.2208 gave 0.4418 CO<sub>2</sub> and 0.0810 H<sub>2</sub>O. C = 54.57; H = 4.07.

0.2940 „ 0.2770 AgBr. Br = 40.07.

C<sub>9</sub>H<sub>7</sub>Br requires C = 55.39; H = 3.58; Br = 41.02 per cent.

This substance is, therefore, *monobromindene*, and its constitution must be represented by the formula  $C_6H_3Br < \begin{smallmatrix} CH \\ CH_2 \end{smallmatrix} > CH$ , because, when oxidised with nitric acid, it yields a monobromophthalic acid.

*Oxidation of Monobromindene.*—In carrying out the oxidation of bromindene, the oil was mixed with about 20 times its volume of ordinary nitric acid, an equal bulk of water added, and the whole gently warmed. As soon as the mixture began to boil, the oil became dark coloured, and quantities of red fumes were evolved. After boiling for three hours, with the occasional addition of small quantities of strong nitric acid, the oil had disappeared, and a yellow solution was obtained; this, on evaporation on a water bath, deposited a viscid, gummy residue, which became quite hard when cold. This was dissolved in water, the solution allowed to evaporate over sulphuric acid in a vacuum, and the crystalline cake which formed, after being freed from oily impurity by spreading it on a porous plate, was repeatedly recrystallised from strong nitric acid, and from fuming hydrobromic acid. In this way a colourless, crystalline mass was obtained, which melted at 161–162°, and decomposed at a slightly higher temperature into water and the anhydride mentioned below. The analysis of this substance showed that it was a bromophthalic acid.

0.1805 gave 0.2587 CO<sub>2</sub> and 0.0362 H<sub>2</sub>O. C = 39.09; H = 2.22.

0.2704 „ 0.2081 AgBr. Br = 32.80.

C<sub>6</sub>H<sub>3</sub>Br(COOH)<sub>2</sub> requires C = 39.18; H = 2.04; Br = 32.66 p. c.

The anhydride of this acid was prepared by heating it at 200°, until all evolution of gas had ceased, and then repeatedly recrystallising the residue from boiling light petroleum (60–80°). The beautiful leafy crystals thus obtained melted sharply at 106°, and gave the following numbers on analysis.

0.1517 gave 0.1248 AgBr. Br = 35.01.

$C_6H_3Br < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > O$  requires Br = 35.24 per cent.

This bromophthalic acid is probably identical with  $\alpha$ -bromophthalic acid [COOH : COOH : Br = 1 : 2 : 4] obtained by Nourrisson (*Ber.*, **20**, 1017) by the oxidation of parabromorthotoluic acid, C<sub>6</sub>H<sub>3</sub>Br(CH<sub>3</sub>)·COOH, [COOH : CH<sub>3</sub> : Br = 1 : 2 : 4]. The melting point of this acid is 168°, and it gives an anhydride melting at 106–108°. It is, however, also possible that it is identical with orthobromophthalic acid, [COOH : COOH : Br = 1 : 2 : 3], melting at 156–158°, which

Racine (*Annalen*, **239**, 76) obtained by the oxidation of orthobrom-orthotoluic acid [ $\text{COOH} : \text{CH}_3 : \text{Br} = 1 : 2 : 6$ ], and the anhydride of which melts at  $95^\circ$ .

In any case the formation of a bromophthalic acid proves that the bromine atom in bromindene is situated in the benzene ring.

*Chemical Laboratory,*

*The Owens College, Manchester.*



SOME DERIVATIVES OF PROPIONIC ACID,  
OF ACRYLIC ACID, AND OF GLUTARIC  
ACID.

BY

WILLIAM HENRY PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1896.]

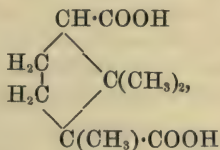




Some derivatives of propionic acid, of acrylic acid, and of glutaric acid.

By WILLIAM HENRY PERKIN, jun.

THESE researches originated in an attempt to prepare synthetically an acid of the formula



which Bredt (*Ber.*, 1893, **26**, 3049) first proposed as being a very probable expression of the constitution of camphoric acid.

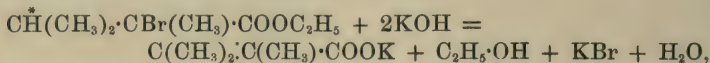
The starting point selected was  $\alpha\beta\beta$ -trimethylpropionic acid (methylisopropylacetic acid), and this was prepared by a method already described by Romburgh (*Rec. Trav. Chim.*, 1886, **5**, 236), namely, the distillation of methylisopropylmalonic acid.



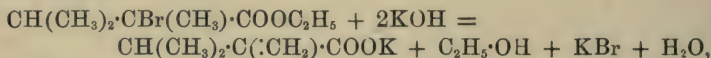
The very carefully purified acid was then converted into *ethylic*  $\alpha$ -bromotrimethylpropionate,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CBr}(\text{CH}_3) \cdot \text{COOC}_2\text{H}_5$ , by first treating it with phosphorus and bromine (Hell, *Ber.*, 1881, **14**, 891; Volhard, *Annalen*, 1887, **242**, 161), and subsequently pouring the product into absolute alcohol.

If now this ethereal salt were treated with alcoholic potash, it should yield an unsaturated acid,  $\text{C}_6\text{H}_{10}\text{O}_2$ , and in the formation of this acid it was anticipated that the elimination of hydrogen

bromide would take place between the bromine atom and the  $\beta$ -hydrogen atom marked \* thus:

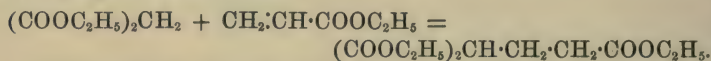


with formation of  $\alpha\beta\beta$ -trimethylacrylic acid, and not between the bromine atom and a hydrogen atom of the  $\alpha$ -methyl group, to form  $\alpha$ -isopropylacrylic acid,

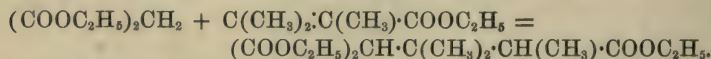


because it is generally found that the hydrogen atom in the CH of the isopropyl group reacts much more readily than the hydrogen atoms in methyl or ethyl groups.

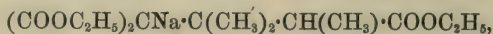
Now, as Auwers and many others have shown, the ethereal salts of  $\alpha\beta$ -unsaturated acids readily condense with the sodium derivative of ethylic malonate, forming additive products; for example, in the case where ethylic acrylate is employed, the substance formed is ethylic propanetricarboxylate:



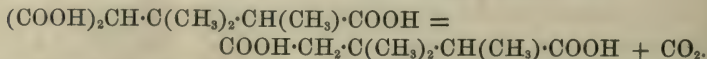
As this reaction takes place in all the cases which have so far been investigated, it seemed probable that if ethylic trimethylacrylate were digested in alcoholic solution with the sodium derivative of ethylic malonate, a similar condensation would take place, and that *ethylic trimethylpropanetricarboxylate* would be formed, thus:



This ethereal salt would be a most interesting substance in many ways, as, apart from the capability, which it would possess, of forming a sodium compound,

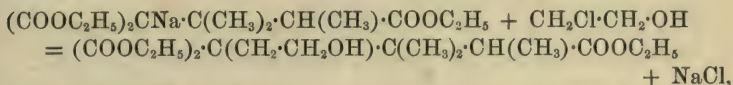


and its consequent value in synthetical work, it would, on hydrolysis, yield a tribasic acid, which, when heated, would lose 1 mol. of carbon dioxide, with formation of  $\alpha\beta\beta$ -trimethylglutaric acid.



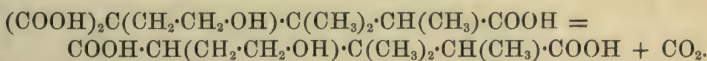
It would be very interesting to synthesise this acid, in order to compare the synthetical acid with an acid which L. Balbiano (*Ber.*, 1895, **28**, 1507) obtained from a product of the oxidation of camphoric acid with cold potassium permanganate, and which this chemist considers to be  $\alpha\beta\beta$ -trimethylglutaric acid.

In using ethylic trimethylpropanetricarboxylate for the synthesis of camphoric acid, it was next proposed to treat its sodium derivative with ethylene chlorhydrin, in order in this way to prepare *ethylic hydroxyethyltrimethylpropanetricarboxylate*, thus:

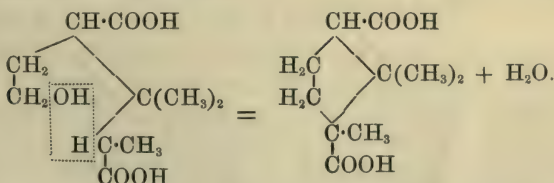


a decomposition which might be expected to proceed in this way, since a strictly analogous reaction, namely, the synthesis of ethylic hydroxyethylacetoacetate,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})\cdot\text{COOC}_2\text{H}_5$ , by the interaction of ethylene chlorhydrin with the sodium compound of ethylic acetoacetate, has been accomplished by Chanlarow (*Annalen*, 1884, **226**, 326).

On hydrolysing the ethereal salt thus obtained, the corresponding tribasic acid would be formed, and this, as it is a derivative of malonic acid, should, when carefully heated, lose 1 mol. of carbon dioxide, with formation of *hydroxyethyltrimethylglutaric acid*.



Lastly, as Bredt's formula for camphoric acid represents this substance as containing a 5-carbon ring, and as this ring is generally produced with great ease, it seemed possible that, by treatment with dehydrating agents, or by other means, an acid of this formula might be formed by the simple elimination of water from hydroxyethyltrimethylglutaric acid, thus:



In investigating the various reactions described above, very unexpected difficulties were met with, necessitating a very careful examination of the methods of preparation and behaviour of a large number of interesting substances which had not previously been prepared, and I beg now to lay before the Society an account of some of the experiments which have, so far, been carried out, reserving the description of the others for a future occasion.

As preliminary experiments soon showed that the preparation of pure  $\alpha\beta\beta$ -trimethylpropionic acid,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ , in quantity required much time, and was a matter of considerable diffi-



culty, and as the preparation is a very expensive one, it was thought best, in the first place, to experiment with isovaleric acid ( $\beta\beta$ -dimethylpropionic acid),  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , in order to discover the conditions which would probably be most favourable for the subsequent work with the trimethyl acid.

Pure isovaleric acid was brominated in the presence of phosphorus in the usual way, and the product converted into ethylic  $\alpha$ -bromovalerate,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CHBr} \cdot \text{COOC}_2\text{H}_5$ , by treatment with alcohol, the conditions for obtaining the best yield being carefully determined.

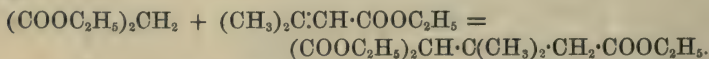
In order now to eliminate hydrogen bromide from this brominated ethereal salt, it was either hydrolysed by means of alcoholic potash,



or digested with quinoline (compare Weinig, *Annalen*, 1894, **280**).

In the first case, dimethylacrylic acid is at once obtained, whereas, in the second case, its ethereal salt is produced, and as in the subsequent experiments the latter was nearly always required, the second method was most frequently employed. Dimethylacrylic acid has already been described by various investigators (see p. 1469): it is a beautifully crystalline acid, which melts at  $70^\circ$ ; ethylic dimethylacrylate is a colourless oil and boils at  $155^\circ$ .

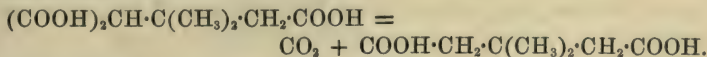
The condensation of ethylic dimethylacrylate with the sodium derivative of ethylic malonate was next investigated, and found to proceed normally, ethylic dimethylpropanetricarboxylate being formed, thus:



But the determination of the conditions for obtaining the best yield of this condensation product gave a considerable amount of trouble, as, in working under the conditions usually employed, only a very small yield of the substance is obtained;\* ultimately, however, a method was devised by which it is possible to prepare considerable quantities of this ethereal salt. Ethylic dimethylpropanetricarboxylate is a colourless oil, which boils at  $203^\circ$  (60 mm.); on hydrolysis,

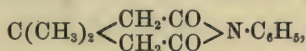
\* An abstract of this work on ethylic dimethylpropanetricarboxylate containing a description of  $\beta\beta$ -dimethylglutaric acid and some of its derivatives, appeared some time since in the *Proceedings* (W. Goodwin and W. H. Perkin, jun., 1894, 64). Auwers (*Ber.*, 1895, **28**, 1130; *Annalen*, 1896, **292**, 145), not knowing of this publication, subsequently investigated the same subject, and obtained results which confirm, in a welcome way, those described here. Auwers also noticed that the yield of ethylic dimethylpropanetricarboxylate, obtained by condensing ethylic dimethylacrylate with the sodium derivative of ethylic malonate under the ordinary conditions, was very small, being only about 8 per cent. of the theoretical.

it yields the corresponding tribasic acid (m. p.  $173^{\circ}$ ), and this, when heated at  $200^{\circ}$ , loses carbon dioxide, with formation of  $\beta\beta$ -dimethylglutaric acid.



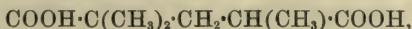
This melts at  $101^{\circ}$ , and, when treated with acetic anhydride, is converted into the anhydride,  $\text{C}(\text{CH}_3)_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix}\rangle\text{O}$ , which melts at  $124^{\circ}$ , or  $23^{\circ}$  higher than the acid itself, a very unusual thing, and especially interesting when it is remembered that camphoric acid, which is supposed by Bredt to be a derivative of dimethylglutaric acid, yields an anhydride which melts  $29$ — $30^{\circ}$  higher than the acid itself does.

Dimethylacrylic acid yields a well characterised anilic acid,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  (m. p.  $134^{\circ}$ ), and this, at its boiling point, is converted into the corresponding anil,



which melts at  $156$ — $157^{\circ}$ .

One of the most remarkable points in connection with this acid is its abnormally high dissociation constant, the value found by Dr. James Walker being  $K = 0.0200$ . Dr. Pfaff subsequently examined the acid obtained by Auwers and Avery (*Annalen*, 1896, **292**, 147), and confirmed the above result, his determination giving the value  $K = 0.0220$ . The dissociation constants in the glutaric series generally vary between  $0.0050$  and  $0.0060$ , the only other exception to this rule, which has so far been observed, being, as Auwers points out, the  $\alpha\alpha\alpha$ -trimethylglutaric acid,



which has the low dissociation constant  $K = 0.0035$ .

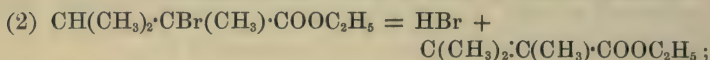
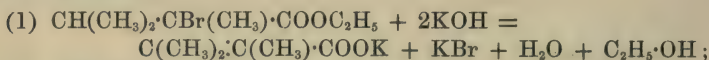
This point is again interesting in view of the possible connection between camphoric acid and  $\beta\beta$ -dimethylglutaric acid, but in this respect the values for the two acids are widely different, the dissociation constant of camphoric acid ( $K = 0.00225$ ) being abnormally low.

While the above experiments were in progress and nearly completed, a similar series of reactions, starting with  $\alpha\beta\beta$ -trimethylpropionic acid,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ , in the place of isovaleric acid, were being pushed forward.

In the first place, this acid was treated with bromine in the presence of phosphorus, under the same conditions as those employed in

the case of isovaleric acid, and the product was decomposed by the addition of alcohol. In this way a very good yield of *ethylic  $\alpha$ -bromo- $\alpha\beta\beta$ -trimethylpropionate*,  $\text{CH}(\text{CH}_3)_2\cdot\text{CBr}(\text{CH}_3)\cdot\text{COOH}$ , was obtained as a colourless oil boiling at  $130^\circ$  (100 mm.) without decomposition.

This ethereal salt, on hydrolysis with alcoholic potash, or when digested with quinoline, behaved, to all appearance, exactly as described above in the case of *ethylic bromisovalerate*, yielding, in the first instance, an oily acid boiling at  $204\text{--}205^\circ$ , and, in the second case, an ethereal salt boiling, not very constantly, at  $162\text{--}167^\circ$ ; and for a long time it was believed that these reactions proceeded in the following manner:



that the acid was, in fact, *trimethylacrylic acid*, and the ethereal salt *ethylic trimethylacrylate*.

As the work progressed it was, however, soon seen that it was most important to be perfectly sure that the constitution of these substances is that given above, and this was found to be a difficult matter, and entailed many months' work.

A quantity of the acid boiling at  $200\text{--}205^\circ$  was prepared by the hydrolysis of *ethylic bromotrimethylpropionate*, and also by the hydrolysis of the ethereal salt produced by digesting this bromo-ethereal salt with quinoline, the oily acid obtained in both cases apparently having the same composition. When this oily acid is allowed to stand for a long time in a cool place, it gradually deposits thick prismatic crystals; these were collected and purified by recrystallisation; they then melted at  $70\text{--}71^\circ$ , and were subsequently proved to consist of pure  *$\alpha\beta\beta$ -trimethylacrylic acid*,  $\text{C}(\text{CH}_3)_2\cdot\text{C}(\text{CH}_3)\cdot\text{COOH}$ . This acid combines with bromine to form  *$\alpha\beta$ -dibromo- $\alpha\beta\beta$ -trimethylpropionic acid*,  $\text{CBr}(\text{CH}_3)_2\cdot\text{CBr}(\text{CH}_3)\cdot\text{COOH}$  (m. p.  $191^\circ$ ); with hydrogen bromide it yields  *$\beta$ -bromotrimethylpropionic acid*,



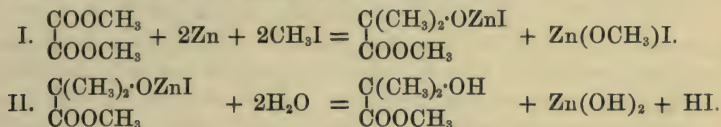
(m. p.  $88^\circ$ ), and with hydrogen iodide,  *$\beta$ -iodotrimethylpropionic acid* (m. p.  $82^\circ$ ); the formation of these substances, which takes place almost quantitatively in each case, was used as a means of characterising and identifying the acid.

In order to prove that the above acid was in reality *trimethylacrylic acid*, it was necessary to prepare it by some method which left no doubt as to its constitution, and this was ultimately accom-

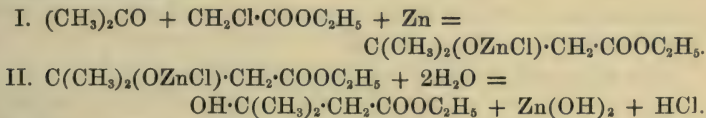


plished by employing a reaction which was first devised by Frankland and Duppa, and which has lately come into some prominence owing to the researches of Reformatsky and others.

Frankland and Duppa showed that  $\alpha$ -hydroxy-derivatives of the fatty acids may be prepared synthetically by the action of zinc on a mixture of methylic oxalate and an alkylic haloïd; methylic hydroxy-isobutyrate, for example, is formed when zinc acts on a mixture of methylic oxalate and methylic iodide (*Annalen*, 1865, **133**, 80); this reaction may be conveniently represented thus:

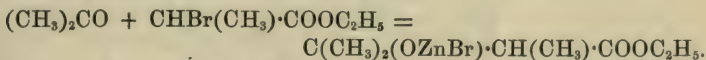


Reformatsky (*Journal of the Russian Chemical Society*, 1890, **22**, 49) subsequently extended this reaction to ketones and ethereal salts of  $\alpha$ -halogen fatty acids, and succeeded in this way in synthesising  $\beta$ -hydroxy-fatty acids. As an example of this important method, the action of zinc on a mixture of acetone and ethylic monochloracetate may be given.

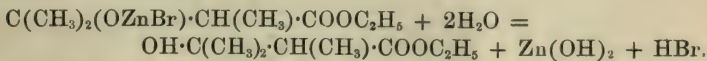


With the aid of this reaction, trimethylacrylic acid may be prepared in a way which clearly proves its constitution, and in carrying out the experiment on this point, I was fortunate in having the assistance of Dr. J. F. Thorpe.

When a mixture of acetone and ethylic  $\alpha$ -bromopropionate is treated with zinc, under suitable conditions, condensation readily takes place, with formation of a peculiar zinc compound, the reaction evidently proceeding in the following way:



This zinc compound is decomposed, on treatment with water and dilute sulphuric acid, with formation of *ethylic  $\beta$ -hydroxy- $\alpha\beta$ -trimethylpropionate*, a thick, colourless oil which distils at  $105^\circ$  (30 mm.) without decomposing.



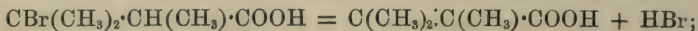
This ethereal salt, on hydrolysis, yields the corresponding hydroxy-acid, a colourless oil which distils at  $160^\circ$  (35 mm.), and which is



very readily acted on by concentrated aqueous hydrobromic and hydriodic acids, yielding  $\beta$ -bromotrimethylpropionic acid,

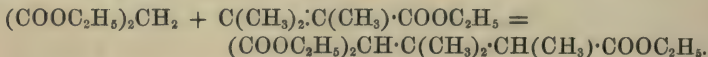


and  $\beta$ -iodotrimethylpropionic acid respectively, substances which are identical with the acids already mentioned as being produced by the addition of hydrogen bromide and hydrogen iodide to trimethylacrylic acid. Lastly, trimethylacrylic acid (m. p.  $70^\circ$ ) is obtained when  $\beta$ -bromotrimethylpropionic acid is treated with alcoholic potash,



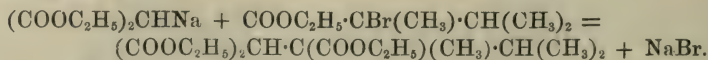
and as this same acid is also formed by the elimination of hydrogen bromide from  $\alpha$ -bromotrimethylpropionic acid, it can only have the constitution represented by the formula  $\text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3) \cdot \text{COOH}$ .

These experiments proved conclusively that the ethereal salt formed by the action of quinoline on ethylic  $\alpha$ -bromotrimethylpropionate as described above, consists, certainly in part, of ethylic trimethylacrylate, and for a long time it was thought that it was composed wholly of this compound. On this assumption, the experiments on the condensation of this ethereal salt with the sodium compound of ethylic malonate were proceeded with, and a condensation product was obtained, which was naturally supposed to be *ethylic trimethylpropanetricarboxylate*,



Unfortunately the yield of this new substance is very small, much smaller, indeed, than the yield of ethylic dimethylpropanetricarboxylate from ethylic dimethylacrylate, and a large number of experiments carried out under the most varying conditions failed to increase the yield to more than about 10 per cent. of the theoretical.

The substances used in this reaction are so difficult to prepare that it was almost impossible to continue the experiments unless the yield of condensation product could be considerably increased, and in order to get over the difficulty, experiments on the action of ethylic  $\alpha$ -bromotrimethylpropionate on the sodium derivative of ethylic malonate were next instituted. In this decomposition, which takes place readily, it was, of course, possible that the two substances would react normally, with formation of ethylic methylisopropylethanetricarboxylate, thus—

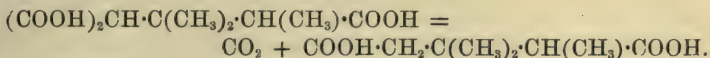


but, judging from the behaviour of other  $\alpha$ -bromo-ethereal salts, such as, for example, ethylic  $\alpha$ -bromoisobutyrate,  $\text{CBr}(\text{CH}_3)_2 \cdot \text{COOC}_2\text{H}_5$ , under similar circumstances, it seemed probable that the reaction

would take place in two stages, that is, that ethylic trimethylacrylate,  $C(CH_3)_2 \cdot C(CH_3) \cdot COOC_2H_5$ , would be first formed by the elimination of hydrogen bromide, and that this unsaturated ethereal salt would then condense with the ethylic malonate present to form ethylic trimethylpropanetricarboxylate, as explained above.

It was thought likely that, at the moment of formation, the ethylic trimethylacrylate might condense more readily with the ethylic malonate, and give a larger yield of condensation product. Both these assumptions were found to be correct, as not only did a careful comparison of the product obtained prove that it was identical with the condensation product obtained on digesting the sodium derivative of ethylic malonate with the supposed ethylic trimethylacrylate as described above;\* but the yield was also considerably larger, being, indeed, sometimes considerably over 20 per cent. of the theoretical, and as this method of preparation involves fewer operations, and therefore requires much less time, it was used in all subsequent preparations of this ethereal salt.

In the course of a careful investigation of the condensation product obtained by either of the above methods, several facts came to light which made it doubtful whether, after all, the substance was really ethylic trimethylpropanetricarboxylate. The condensation product, on hydrolysis, yields a beautifully crystalline tribasic acid, which, when heated at  $200^\circ$ , readily loses 1 mol. of carbon dioxide, with formation of a crystalline dibasic acid, which should be  $\alpha\beta\beta$ -trimethylglutaric acid.



The acid thus produced is very similar to the acid which Balbiano (*Ber.*, 1895, **28**, 1507) obtained from camphoric acid, and which is very probably  $\alpha\beta\beta$ -trimethylglutaric acid; the former melts at  $94-95^\circ$ , and gives an anilic acid, melting at  $158-159^\circ$ , whereas the latter melts at  $89^\circ$ , and yields an anilic acid melting at  $150^\circ$ , but the anhydrides of the two acids differ considerably, that from the acid obtained by me melting at  $53^\circ$ , whereas the anhydride of Balbiano's acid melts at  $80-81^\circ$ .

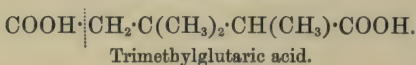
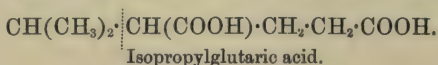
But, because the acid is not identical with Balbiano's acid, it does not prove that it is not  $\alpha\beta\beta$ -trimethylglutaric acid, for the reason that the constitution of Balbiano's acid is not known with certainty;

\* These experiments were conducted, in the usual manner, in alcoholic solution; in xylene solution, also, the reaction proceeds in the same way, which is rather remarkable, as usually the unsaturated intermediate substance is not so readily formed from  $\alpha$ -bromo-ethereal salts under these conditions, the product consisting, at all events to a large extent, of the normal ethane derivative.

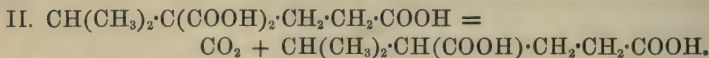
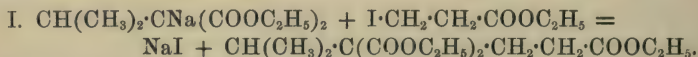
the latter might, for example, quite well be  $\alpha\alpha\beta$ -trimethylglutaric acid,  $\text{COOH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{COOH}$ , nevertheless it seemed desirable to further investigate the subject, and, as the result, it was ultimately conclusively proved that the synthetical acid is not trimethylglutaric acid, but  $\alpha$ -isopropylglutaric acid,



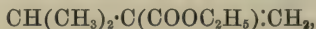
On oxidation with chromic acid the acid yields, besides acetic acid, only succinic acid, whereas from trimethylglutaric acid under these circumstances trimethylsuccinic acid should be formed.



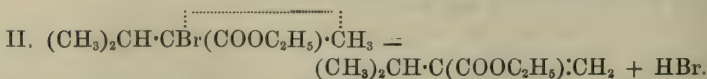
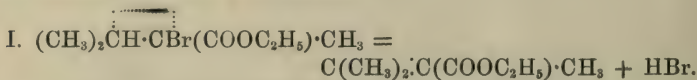
Subsequently it was shown that the acid is identical with the isopropylglutaric acid, which, for the sake of comparison, was synthesised by Mr. Heinke and myself from the product of the action of ethylic  $\beta$ -iodopropionate on the sodium compound of ethylic isopropylmalonate, by hydrolysis and subsequent elimination of carbon dioxide.



A careful re-investigation of the whole matter showed that when ethylic  $\alpha$ -bromotrimethylpropionate is treated with quinoline, the product does not consist entirely of ethylic trimethylacrylate, but is a mixture of this substance with ethylic  $\alpha$ -isopropylacrylate,

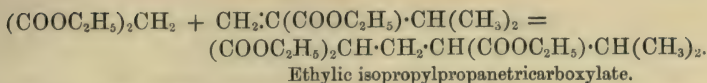


the elimination of hydrogen bromide from the brom-ethereal salt having taken place in two directions.



When these mixed ethereal salts are digested with the sodium derivative of ethylic malonate, the ethylic isopropylacrylate *alone* enters into the reaction.





The ethylic trimethylacrylate takes apparently\* *no part* in the condensation, and, indeed, the latter substance may be, at all events, partially recovered from the product of the action.

This behaviour of ethylic trimethylacrylate is very remarkable, and, so far, without parallel; very probably the further investigation of the condensation of  $\alpha\beta$ -unsaturated ethereal salts with the sodium derivatives of ethylic malonate and allied compounds will show the nature and number of the groups, which, when attached to the double band, render the condensation a matter of difficulty, or, in some cases, prevent it altogether.

During the course of these experiments, and while it was thought that the condensation product described above had the constitution,  $(\text{COOC}_2\text{H}_5)_2\text{CH}\dagger\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$ , experiments were being made on the introduction of the group  $-\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , at the point marked †, for the reasons given at the commencement of this paper. These experiments were not in the first instance actually made with this condensation product, owing to the great difficulty of obtaining it in any quantity, but with somewhat similarly constituted substances which could be more readily prepared. Arguing from the results of Chanlarow's experiments on the action of ethylene chlorhydrin on the sodium derivative of ethylic acetoacetate (*Annalen*, 1884, **226**, 326), it seemed probable that the best way of achieving the object in view would be to treat the sodium compound of this condensation product with ethylene chlorhydrin, but although many experiments were made on the action of this substance on the sodium derivatives of ethylic methylmalonate, ethylic isopropylmalonate, and on the corresponding mono-substitution derivatives of ethylic acetoacetate, in no case could more than traces of the hydroxyethyl substitution product be isolated, the unaltered ethereal salt being in all cases recovered almost quantitatively.

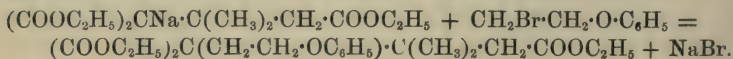
This want of success led to the investigation of the action of  $\gamma$ -phenoxyethylic bromide,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , on the sodium derivatives of ethylic malonate, ethylic methylmalonate, and similarly constituted compounds; a description of these experiments, all of which gave satisfactory results, has already appeared in the *Transac-*

\* A careful examination of the mother liquors from the crystallisation of the isopropylpropanetricarboxylic acid resulting from the hydrolysis of the ethylic salt produced by the condensation failed to reveal the presence of even traces of trimethylpropanetricarboxylic acid. This acid may, nevertheless, of course have been present in small quantity and have escaped detection.



tions of this Society (W. H. Bentley, E. Haworth, and W. H. Perkin, jun., 1896, **69**, 161).

While this preliminary work was in progress, the action of phenoxyethylic bromide and sodium ethoxide on ethylic dimethylpropanetricarboxylate was being investigated, because this ethereal salt is much more readily prepared than the substance now known to be ethylic isopropylpropanetricarboxylate. In this case it was expected that the reaction would proceed thus.

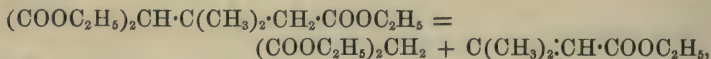


But on hydrolysing the product, an acid was obtained, which was not derived from an ethereal salt of this constitution; this was subsequently shown to be diphenoxyethylmalonic acid,



and identical with the acid obtained by the action of phenoxyethylic bromide and sodium ethoxide on ethylic malonate (Trans., 1896, **69**, 169), a reaction which was, in fact, studied in order to prove the identity of the two acids.

It seems probable that during the course of the above reaction the ethylic dimethylpropanetricarboxylate undergoes, in the first instance, partial decomposition into ethylic malonate and ethylic dimethylacrylate,

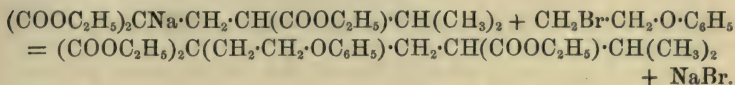


a kind of decomposition which has been observed in other cases, but which is particularly remarkable in the present instance as being the exact reverse of the process which results in the formation of the ethereal salt, namely, by the condensation of ethylic malonate with ethylic dimethylacrylate in the presence of sodium ethoxide. The regenerated ethylic malonate then reacts with the phenoxyethylic bromide and sodium ethoxide, with formation of ethylic diphenoxyethylmalonate,  $(\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{C}(\text{COOC}_2\text{H}_5)_2$ .

At first sight it would seem more likely that ethylic phenoxyethylmalonate,  $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$  (this vol., p. 167), would be formed in this way, but probably the decomposition of the ethylic dimethylpropanetricarboxylate into ethylic malonate and ethylic dimethylacrylate is a gradual one, and thus the ethylic malonate would always be in the presence of excess of sodium ethoxide and phenoxyethylic bromide.

Although these experiments did not seem to indicate that there was much chance of the study of the action of phenoxyethylic bromide on the sodium compound of ethylic isopropylpropanetricarb-

oxylate\* giving the desired results, it was nevertheless decided to investigate this point, and the result was certainly unexpected, as the reaction in this case was found to proceed in a perfectly normal manner, thus.

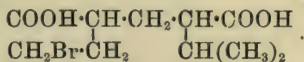


The yield of *ethylic phenoxyethylisopropylpropanetricarboxylate* thus obtained is certainly not good, but there was no indication of a decomposition of the molecule similar to that observed in the case of *ethylic dimethylpropanetricarboxylate*.

On hydrolysing the product of the above reaction, the corresponding tribasic acid is obtained as a beautifully crystalline substance, which melts at  $180^\circ$ , decomposing at the same time into carbon dioxide and phenoxyethylisopropylglutaric acid (m. p.  $93^\circ$ ).



When digested with hydrobromic acid, this acid yields quantities of phenol, and a new crystalline acid, which is probably bromethylisopropylglutaric acid.



This acid and the corresponding hydroxy-acid, which is formed by boiling the bromo-acid with sodium carbonate solution, appear to have very interesting properties, and will be made the subject of a further investigation, the results of which I hope to lay before the Society in a short time.

Some of the experiments described in this paper were carried out with the assistance of Dr. J. F. Thorpe and Mr. W. Goodwin; where this has been the case I have stated the fact at the commencement of the section in question. I beg to thank these gentlemen, and also Messrs. W. H. Bentley, E. Haworth, and J. L. Heinke, for their valuable assistance during the whole course of this investigation.

#### EXPERIMENTAL.

*ββ-Dimethylacrylic acid*,  $\text{C}(\text{CH}_3)_2\text{CH}\cdot\text{COOH}$ . [With W. GOODWIN.]

This acid has already been prepared by Miller (*Annalen*, 1881, 206, 261) by the elimination of water from *β*-hydroxyisobutylformic

\* This was of course supposed at the time to be *ethylic trimethylpropanetricarboxylate*.

acid,  $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$ , by boiling it with dilute sulphuric acid, and by Duvillier (*Ann. Chim. Phys.*, [5], **19**, 428), by the action of sodium ethoxide on ethylic  $\alpha$ -bromovalerate. Subsequently Weinig (*Annalen*, 1894, **280**, 253) showed that a good yield of ethylic dimethylacrylate may be obtained by boiling ethylic  $\alpha$ -bromovalerate with diethylaniline.

In our experiments, we used one of the two following processes, according as we required the free acid or its ethereal salt.

1. The hydrolysis of ethylic  $\alpha$ -bromovalerate with alcoholic potash.
2. The removal of hydrogen bromide from ethylic  $\alpha$ -bromovalerate by means of quinoline.

*Method I. Preparation of Dimethylacrylic acid.*—Potash (100 grams) is dissolved in a small quantity of boiling 80 per cent. alcohol, the solution heated on a water bath in a flask connected with a reflux condenser, and then pure ethylic  $\alpha$ -bromoisovalerate (100 grams) added as rapidly as possible through the condenser. As soon as the very vigorous action has subsided, the heating is continued for about half an hour; water is then added, the clear brownish solution evaporated until free from alcohol, acidified, and extracted three times with pure ether.

The ethereal extract is dried over calcium chloride, the ether distilled off, and the residue fractionated under the ordinary pressure, when nearly the whole passes over between  $185^\circ$  and  $195^\circ$  as a colourless oil which, on standing, becomes completely filled with long, colourless crystals. These were freed from adhering oil by means of the pump, and purified by recrystallisation from light petroleum (b. p.  $50$ — $60^\circ$ ); the oily mother liquor from the crystals, on careful fractionation, yields more of the crystalline acid; ultimately a considerable quantity of an unpleasant smelling, oily liquid is left which does not crystallise at ordinary temperatures, and the nature of which we have not investigated.

Dimethylacrylic acid crystallises from light petroleum in long, colourless needles which melt at  $69^\circ$ , and are readily soluble in alcohol, ether, and hot, light petroleum, sparingly soluble in water. The analysis of the acid gave the following results.

- I. 0.1439 gave 0.3164  $\text{CO}_2$  and 0.1040  $\text{H}_2\text{O}$ . C = 59.97; H = 8.02.  
 II. 0.1600 „ 0.3495 „ „ 0.1157 „ C = 59.56; H = 8.03.  
 $\text{C}_5\text{H}_8\text{O}_2$  requires C = 60.00; H = 8.0 per cent.

*Method II. Preparation of Ethylic Dimethylacrylate.*—In the preparation of this ethereal salt, ethylic  $\alpha$ -bromoisovalerate was digested with quinoline instead of with diethylaniline as proposed by Weinig (*Annalen*, 1894, **280**, 253), because it was found that the former reacted more vigorously than the latter, and yielded a product con-



taining only traces of bromine; the whole method requiring much less time than when diethylaniline is employed.

Pure ethylic  $\alpha$ -bromisovalerate, in quantities of 50 grams, is heated in a reflux apparatus with freshly distilled coal tar quinoline (75—100 grams), a thermometer being placed in the liquid to allow of the temperature being observed. At about 170—175°, and as soon as the reaction sets in, the flame is removed; the whole boils gently for some time, the temperature rising spontaneously to 190°. As soon as the action has subsided, the liquid is heated at 185—190° for 10 minutes, the dark brown product poured into excess of dilute hydrochloric acid, extracted with ether, the ethereal solution washed with hydrochloric acid, dried over calcium chloride, and the ether distilled off.

If the ethereal salt is required free from bromine, it is again heated with about half its weight of quinoline in the same manner as before, and ultimately carefully fractionated; after three fractionations, almost the whole passes over between 154° and 155° as a colourless oil of penetrating odour. An analysis gave the following results.

0.1530 gave 0.3660 CO<sub>2</sub> and 0.1341 H<sub>2</sub>O. C = 65.24; H = 9.43.

C<sub>7</sub>H<sub>12</sub>O<sub>2</sub> requires C = 65.62; H = 9.37 per cent.

When digested with excess of potash in methyl alcoholic solution, ethylic dimethylacrylate is completely hydrolysed in less than one hour; it is not necessary to digest for 12—14 hours, as Weinig (*loc. cit.*, p. 254) states. In order to isolate the dimethylacrylic acid, the product of the hydrolysis is evaporated with water until free from alcohol, acidified, extracted with ether, and purified as described under Method I.

The ethylic dimethylacrylate used in this research was prepared partly by the action of quinoline on ethylic  $\alpha$ -bromisovalerate, as described above, and partly by the etherification of pure dimethylacrylic acid. In the latter case, the pure acid (50 grams) was dissolved in absolute alcohol (100 grams), concentrated sulphuric acid (50 grams) added, and the whole allowed to stand over night. Water was then added, the ethereal salt extracted with ether, the ethereal solution washed with water and dilute sodium carbonate solution, dried over anhydrous potassium carbonate, and the ether distilled off. The residual ethereal salt, on fractionation, distilled almost constantly at 154—155°, but it did not give very good results on analysis.

	Found.			Theory. C <sub>7</sub> H <sub>12</sub> O <sub>2</sub> .
	I.	II.	III.	
C.....	65.01	64.91	64.75 p. c.	65.62 p. c.
H .....	9.17	9.21	9.22 „	9.37 „



*Ethylic Dimethylpropanetricarboxylate,*  
 $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ . [With W. GOODWIN.]

In order to prepare this substance, pure ethylic dimethylacrylate was digested in alcoholic solution with excess of the sodium derivative of ethylic malonate, the quantities usually employed being the following.

Ethylic malonate .....	160	grams
Sodium       ,,       .....	23	,,
Alcohol       ,,       .....	250	,,
Ethylic dimethylacrylate ...	80	,,

The sodium was dissolved in the alcohol, the slightly warm solution mixed with the ethylic malonate, the ethylic dimethylacrylate then added, and the whole heated in a reflux apparatus (or, in some cases, in soda-water bottles) for eight hours at  $60^\circ$ , and then for eight hours on a water bath. The opaque, slightly brownish product was mixed with water and dilute hydrochloric acid, extracted twice with ether, the ethereal solution well washed with water and dilute hydrochloric acid, dried over calcium chloride, evaporated, and the residual oil purified by fractionation under reduced pressure (60 mm.).

After a considerable quantity of unchanged ethylic dimethylacrylate and ethylic malonate had passed over, the thermometer rose rapidly to  $195^\circ$ , almost the whole of the residue distilling between this temperature and  $210^\circ$ .

Pure ethylic dimethylpropanetricarboxylate distils at  $203^\circ$  (60 mm.). Auwers (*loc. cit.*, p. 113) found the boiling point to be  $194^\circ$  (43 mm.); he does not appear, however, to have analysed his product. The analyses of the ethereal salt prepared by us gave the following results.

- I. 0.132 gave 0.2809  $\text{CO}_2$  and 0.0986  $\text{H}_2\text{O}$ .   C = 58.00; H = 8.30.  
 II. 0.158   ,,   0.3375   ,,   ,,   0.1183   ,,   C = 58.25; H = 8.32.  
 $\text{C}_{14}\text{H}_{24}\text{O}_6$  requires C = 58.33; H = 8.33 per cent.

Ethylic dimethylpropanetricarboxylate is a moderately thick, colourless oil, which, when heated in small quantities, distils under the ordinary pressure almost without decomposition.

The yield of this ethereal salt, obtained under the above conditions, varied considerably in different experiments, amounting, as it did in more than one case, to over 40 per cent. of theory, whilst in one or two cases the yield was as low as 21 per cent. Auwers, in his experiments on the condensation of ethylic dimethylacrylate with ethylic malonate in alcoholic solution, obtained only 8 per cent. of the theoretical yield of this ethereal salt; but he worked under different conditions from those we employed.

*Dimethylpropanetricarboxylic acid*,  $(\text{COOH})_2\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOH}$ .

In order to prepare this acid, 20 grams of pure ethylic dimethylpropanetricarboxylate, in methyl alcoholic solution, was digested with excess of potash (20 grams) for two hours in a reflux apparatus. The solution was then mixed with water, concentrated on a water bath, boiled until quite free from alcohol, cooled well, acidified, and extracted 20 times with ether. The ethereal solution, after drying over calcium chloride, was evaporated, and the residue allowed to stand over sulphuric acid in a vacuum desiccator until it had almost completely solidified.

After standing for six days in contact with porous porcelain, the crystals, which were colourless and free from oil, were dissolved in a little water, and the solution filtered and saturated with hydrogen chloride, the whole being well cooled during the operation. The acid soon commenced to separate in sandy crystals, which, after 24 hours, were collected, drained on a porous plate, dried at  $100^\circ$ , and analysed with the following results.

0.1501 gave 0.2585  $\text{CO}_2$  and 0.0815  $\text{H}_2\text{O}$ .  $\text{C} = 46.99$ ;  $\text{H} = 6.04$ .

$\text{C}_8\text{H}_{12}\text{O}_6$  requires  $\text{C} = 47.06$ ;  $\text{H} = 5.88$  per cent.

*Dimethylpropanetricarboxylic acid* softens at  $168^\circ$ , and decomposes at  $173^\circ$  with rapid evolution of carbon dioxide. It is readily soluble in water and alcohol, much less so in ether, and only very sparingly in hydrochloric acid, so that when its concentrated aqueous solution is saturated with hydrogen chloride the acid separates almost completely. The pure substance is very stable, and may be heated at  $100^\circ$  for a considerable time without appreciable decomposition.

*Salts*.—A neutral solution of the ammonium salt of the acid gives no precipitate with *copper sulphate* or with *barium* or *calcium chlorides*; but on the addition of *lead acetate*, a voluminous gelatinous precipitate is produced.

The *silver salt*,  $\text{C}_8\text{H}_9\text{O}_6\text{Ag}_3$ , was prepared by adding silver nitrate to a slightly alkaline solution of the ammonium salt; it is a white, curdy precipitate, insoluble in water. After well washing and drying, first over sulphuric acid and then at  $100^\circ$ , the following results were obtained on analysis.

I. 0.1809 gave on ignition 0.1108 Ag.  $\text{Ag} = 61.26$ .

II. 0.2159 „ „ 0.1325 „  $\text{Ag} = 61.37$ .

$\text{C}_8\text{H}_9\text{O}_6\text{Ag}_3$  requires  $\text{Ag} = 61.71$  per cent.

*$\beta\beta$ -Dimethylglutaric acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOH}$ .

[With W. GOODWIN.]

This acid is formed when dimethylpropanetricarboxylic acid is

heated above its melting point. In carrying out this decomposition quantitatively, the following behaviour was observed.

7.1825 grams of the tribasic acid heated in a wide test tube at  $185-190^{\circ}$  for 3—4 minutes lost 1.6070 gram = 22.4 per cent., but on continuing the heating for half an hour, the loss was 1.92 gram or 26.7 per cent. Theoretically, for the elimination of one molecule of carbon dioxide, the loss should be 21.5 per cent.; this agrees with the results obtained on heating the acid for a short time at  $185-190^{\circ}$ . The further loss on prolonged heating is due to anhydride formation, and, to a small extent, to sublimation.

The residue from this experiment solidified completely on cooling. It was powdered, dissolved in water, and the solution saturated with hydrogen chloride. On standing, beautiful, colourless crystals separated, which, after drying at  $100^{\circ}$ , gave the following results on analysis.

- I. 0.1694 gave 0.3256  $\text{CO}_2$  and 0.1177  $\text{H}_2\text{O}$ .  $\text{C} = 52.42$ ;  $\text{H} = 7.72$ .  
 II. 0.1538 „ 0.2962 „ „ 0.1071 „  $\text{C} = 52.53$ ;  $\text{H} = 7.73$ ,  
 $\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ .  $\text{H} = 7.50$  per cent.

*$\beta\beta$ -Dimethylglutaric acid* is a colourless, crystalline substance which melts at  $101^{\circ}$ . It is very readily soluble in water, alcohol, and ether, but only sparingly in hydrochloric acid, benzene, and light petroleum; it crystallises well from water in colourless needles, but is most readily and economically obtained pure by recrystallisation from hot hydrochloric acid, as described above, as in this way very little remains in the mother liquor.

*Salts of  $\beta\beta$ -Dimethylglutaric acid. Silver Salt,  $\text{C}_7\text{H}_{10}\text{Ag}_2\text{O}_4$ .*—This salt was prepared by adding silver nitrate to the slightly alkaline solution of the ammonium salt. It is a white, insoluble precipitate, which, after well washing with water and drying at  $100^{\circ}$ , gave the following results on analysis.

- I. 0.1608 gave 0.1320  $\text{CO}_2$ , 0.0403  $\text{H}_2\text{O}$ , and 0.093 Ag.  $\text{C} = 22.38$ ;  
 $\text{H} = 2.79$ ;  $\text{Ag} = 57.83$ .  
 II. 0.201 on ignition gave 0.1159 Ag.  $\text{Ag} = 57.66$   
 $\text{C}_7\text{H}_{10}\text{Ag}_2\text{O}_4$  requires  $\text{C} = 22.46$ ;  $\text{H} = 2.66$ ;  $\text{Ag} = 57.76$  per cent.

A neutral solution of the ammonium salt shows the following behaviour with reagents. *Calcium chloride* and *barium chloride* give no precipitate even on boiling. *Copper acetate* gives no precipitate in the cold, but, on boiling, a light blue, apparently crystalline precipitate separates. *Lead acetate* also gives no precipitate in the cold, but, on warming, the solution rapidly becomes turbid, and an amorphous lead salt separates.



*Ethylic Dimethylglutarate*,  $\text{COOC}_2\text{H}_5 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ .

This was prepared by dissolving the pure acid in absolute alcohol, adding concentrated sulphuric acid ( $\frac{1}{2}$  vol.), and allowing the mixture to stand for two days; it was then heated in the water bath for two hours, mixed with water, and the oily ethereal salt extracted with ether. The ethereal extract was washed well with dilute sodium carbonate, dried over anhydrous potassium carbonate, evaporated, and the residual oil purified by distillation under reduced pressure, when almost the whole quantity passed over at  $170\text{--}172^\circ$  (100 mm.).

I. 0.2011 gave 0.4488  $\text{CO}_2$  and 0.1680  $\text{H}_2\text{O}$ . C = 60.89; H = 9.28.

II. 0.1407 „ 0.3126 „ „ 0.1184 „ C = 60.59; H = 9.35.

$\text{C}_{11}\text{H}_{20}\text{O}_4$  requires C = 61.11; H = 9.26 per cent.

Ethylic dimethylglutarate distils, apparently without decomposition, at  $241\text{--}243^\circ$  (755 mm.), or only slightly higher than ethylic glutarate, which boils at  $237^\circ$ ; it has a faint odour somewhat resembling that of ethylic succinate.

*Dimethylglutaric Anhydride*,  $\text{C}(\text{CH}_3)_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{O}$ .

[With W. GOODWIN.]

Dimethylglutaric acid dissolves readily in hot acetic anhydride, and if the solution is heated in a test-tube in a sulphuric acid bath until the excess of acetic anhydride has distilled off, the residue solidifies on cooling to a hard, crystalline cake. The crystals were spread on porous porcelain until free from mother liquor, and dried at  $100^\circ$ ; they then melted at  $124^\circ$ , and, after recrystallisation from acetic anhydride, at  $124\text{--}125^\circ$ ,

I. 0.1376 gave 0.2960  $\text{CO}_2$  and 0.0892  $\text{H}_2\text{O}$ . C = 58.72; H = 7.20.

II. 0.1240 „ 0.2674 „ „ 0.0803 „ C = 58.79; H = 7.19.

$\text{C}_7\text{H}_{10}\text{O}_3$  requires C = 59.16; H = 7.04 per cent.

*Dimethylglutaric anhydride* crystallises from acetic anhydride, in which it is very soluble, in thin plates; these, after drying well between filter paper, smell of acetic anhydride, and become quite sticky in the water oven, and remain so for at least an hour, so that it is possible that these crystals consist of a mixed anhydride of acetic and dimethylglutaric acids, which, on heating, decompose into acetic anhydride and dimethylglutaric anhydride; this point has, however, not been further investigated. Dimethylglutaric anhydride is readily soluble in benzene, but only sparingly in light petroleum (b. p.  $40\text{--}50^\circ$ ), it dissolves, however, in petroleum boiling at  $110\text{--}120^\circ$ , and on cooling crystallises out in plates. It is insoluble in cold water, but on heating it melts under water, and rapidly dissolves.



*Dimethylglutaranilic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , and

*Dimethylglutaranil*,  $\text{C}(\text{CH}_3)_2\left<\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\right>\text{N}\cdot\text{C}_6\text{H}_5$ .

If a solution of dimethylglutaric anhydride in a little benzene is mixed with the calculated quantity of freshly distilled aniline, the mixture gets hot and rapidly begins to deposit crystals; these, after being collected and drained on porous porcelain, are crystallised two or three times from dilute alcohol.

0.1461 gave 7.7 c.c. moist nitrogen at  $17^\circ$  and 756 mm.  $\text{N} = 6.12$ .

$\text{C}_{13}\text{H}_{17}\text{NO}_3$  requires  $\text{N} = 5.96$  per cent.

*Dimethylglutaranilic acid* melts at about  $134^\circ$ , but if slowly heated it softens at about  $128^\circ$  and melts at  $131^\circ$ . It is very readily soluble in alcohol and chloroform, but only sparingly in water, benzene, and light petroleum; it crystallises from dilute alcohol in small, hard, glistening prisms, and very beautifully, in similar form, when its solution in chloroform is allowed to evaporate spontaneously.

*Dimethylglutaranil* is obtained by heating the anilic acid to boiling for 10 minutes, in a test-tube; water is given off, and, on cooling, the residue solidifies completely. After recrystallising twice from dilute alcohol, the anil is obtained pure in colourless, glistening plates, which melt at  $156$ – $157^\circ$ .

0.1380 gave 7.8 c.c. moist nitrogen at  $18^\circ$  and 760 mm.  $\text{N} = 6.52$ .

$\text{C}_{13}\text{H}_{15}\text{NO}_2$  requires  $\text{N} = 6.45$  per cent.

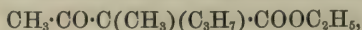
*Dimethylglutaranil* is readily soluble in alcohol, benzene, and chloroform, but only sparingly in water or light petroleum.

*$\alpha\beta$ -Trimethylpropionic acid*,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ .

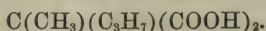
This acid has already been prepared by Markownikoff (*Zeit. f. Chem.*, 1866, 502) from methylisopropylcarbonyl cyanide,



by hydrolysis, and also by Romburgh (*Rec. Trav. Chim.*, 1886, 5, 231) by the hydrolysis of ethylic methyl isopropylacetoacetate,



and by the distillation of methylisopropylmalonic acid,



In preparing large quantities of this acid, I have used exclusively the latter method: as, however, the isolation of the pure acid was found to be a matter of considerable difficulty, I give the method of preparation in full. In the first place, ethylic methylmalonate was prepared by the action of methylic iodide on the sodium derivative of

ethylic malonate\* in alcoholic solution, great care being taken by using a slight excess (about 5 per cent.) of the calculated quantity of sodium, and a considerable excess of methylic iodide, that the product should be as free from ethylic malonate as possible.

In subsequently introducing the isopropyl group into the carefully fractioned ethylic methylmalonate, the following method was found convenient.

Ethylic methylmalonate (345 grams) is mixed with sodium (46 grams) dissolved in alcohol (500 grams) in a large flask connected with a very long reflux condenser; isopropyl bromide (260 grams) is then added, and the whole very gently warmed, the action being kept well under control, otherwise the whole begins to boil very vigorously, and much isopropyl bromide escapes through the condenser.

As soon as the principal reaction is over, the mass is heated to boiling for six hours, the bulk of the alcohol distilled off, water added, and the oil which separates extracted three times with ether; the ethereal solution, after washing well with water and evaporating, deposits a nearly colourless oil, from which, by repeated fractionation, 330 grams, or about 75 per cent. of the theoretical yield of nearly pure ethylic methylisopropylmalonate, boiling at 217—222°, can be obtained.

0.1431 gave 0.3190  $\text{CO}_2$  and 0.1162  $\text{H}_2\text{O}$ .  $\text{C} = 60.80$ ;  $\text{H} = 9.03$ .

$\text{C}_{11}\text{H}_{20}\text{O}_4$  requires  $\text{C} = 61.11$ ;  $\text{H} = 9.26$  per cent.

This ethereal salt was hydrolysed by digesting it for two hours with potash (260 grams) dissolved in purified methylated spirit; water was then added, and the product heated first on a water bath and finally boiled over a free flame till quite free from alcohol; the concentrated solution was then acidified and extracted six times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited about 280 grams of an oily acid, which still contained some ether, and, on standing, rapidly began to crystallise. This crude product was now heated at 180—200° until the evolution of carbon dioxide had ceased, and the residue distilled without, in the first instance, attempting to fractionate.

The crude distillate always contains traces of propionic and isovaleric acids, and it is remarkable that pure methylisopropylacetic acid can only be isolated from this with very considerable difficulty,

\* In carrying out this preparation with large quantities of material, the methylic iodide must be added very cautiously in small quantities to the alcoholic solution of the sodium derivative of ethylic malonate, the whole being well cooled during the operation, otherwise the action is very violent, and if care be not taken, the liquid boils most vigorously, with loss of methylic iodide from volatilisation, and frequently from frothing over.

repeated fractionation from a flask fitted with a long colonna being necessary, in order to effect as complete a separation as possible.

Ultimately, however, about 180 grams of an oil boiling constantly at 189—190° were obtained, which consisted of nearly pure methylisopropylacetic acid, as the following analyses show.

- I. 0.1606 gave 0.3622 CO<sub>2</sub> and 0.1440 H<sub>2</sub>O. C = 61.50; H = 9.96.  
 II. 0.1314 „ 0.2952 „ „ 0.1230 „ C = 61.27; H = 10.34.  
 C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> requires C = 62.07; H = 10.34 per cent.

*Trimethylpropionic acid* is a most disagreeably smelling mobile liquid, which boils at 189—190°. *Romburgh* (*loc. cit.*) found practically the same boiling point, namely, 189—191°.

*Ethyl α-Bromotrimethylpropionate*, CH(CH<sub>3</sub>)<sub>2</sub>·CBr(CH<sub>3</sub>)·COOC<sub>2</sub>H<sub>5</sub>.

The bromination of methylisopropylacetic acid is very readily carried out by treating the acid bromide with bromine according to Volhard's method (*Annalen*, 1887, **242**, 161), and as the result of a number of experiments, the following quantities were found to give the best results.

In a flask, into the neck of which a long condensing tube is ground, methylisopropylacetic acid (50 grams) is mixed with phosphorus pentabromide (75 grams) and allowed to remain for about one hour, until the formation of the acid bromide is complete. Dry bromine (85 grams) is then added in about six portions, the flask being cooled between each addition; the liquid is then heated gradually on a water bath to about 50—60°, until the action is nearly complete, and finally at 100° for two hours.

The well cooled product, which is usually coloured, owing to the presence of a slight excess of bromine, is poured in a thin stream into three times its volume of absolute alcohol, the vigorous action being allowed to proceed without cooling; after standing overnight, water is added, and the bromo-ethereal salt is extracted with ether. The ethereal solution, after washing with water and dilute sodium carbonate solution, drying over calcium chloride, and evaporating, deposits a somewhat brownish oil, which, on fractionating twice under reduced pressure (100 mm.), boils for the most part constantly at 130°, the yield being usually good, although, in one or two cases, not inconsiderable quantities of some higher boiling substance was obtained.

The analysis of the pure substance gave the following result.

0.2035 gram substance, heated with fuming nitric acid and silver nitrate at 180° for four hours, gave 0.1722 gram AgBr = 36.01 per cent. of bromine.

C<sub>8</sub>H<sub>15</sub>BrO<sub>2</sub> requires Br = 35.89 per cent.



*Ethyllic  $\alpha$ -bromotrimethylpropionate* is a heavy, very pungent smelling, colourless oil, very similar to ethyllic  $\alpha$ -bromisovalerate in its general properties.

*Trimethylacrylic acid*,  $C(CH_3)_2 \cdot C(CH_3) \cdot COOH$ .

As stated in the introduction, this acid was first prepared by the hydrolysis of ethyllic methylisopropylbromacetate with alcoholic potash.

Potash (100 grams) was dissolved in the smallest possible quantity of 80 per cent. alcohol in a flask connected with a long reflux condenser, the solution heated on a boiling water bath, and then the pure bromo-etheral salt (100 grams) added as rapidly as possible through the condenser tube. After the very vigorous action had subsided, the whole was heated to boiling for about an hour, water was added, the brown solution evaporated until quite free from alcohol, acidified, and extracted five times with pure ether. The ethereal solution was then dried over calcium chloride, evaporated, and the residue fractionated two or three times under reduced pressure, and subsequently at the ordinary pressure, in order to separate the trimethylacrylic acid as far as possible from a considerable quantity of  $\alpha$ -hydroxytrimethylpropionic acid (p. 1486), which is formed at the same time.

In this way, an oily acid was obtained, boiling constantly at  $204\text{--}205^\circ$  (under 100 mm. pressure it boils at  $150^\circ$ ), and consisting of a mixture of the two isomeric acids, isopropylacrylic acid and trimethylacrylic acid. It gave the following results on analysis.

0.1641 gave 0.3760  $CO_2$  and 0.1320  $H_2O$ .  $C = 62.5$ ;  $H = 8.93$ .

$C_6H_{10}O_2$  requires  $C = 63.15$ ;  $H = 8.77$  per cent.

During the winter months, this oily acid gradually deposited a quantity of beautiful, prismatic, four sided crystals; these were collected with the aid of the pump, drained on porous porcelain, and recrystallised from light petroleum. The new substance was thus readily obtained in a pure state, and gave the following numbers on analysis.

I. 0.1312 gave 0.3014  $CO_2$  and 0.1056  $H_2O$ .  $C = 62.64$ ;  $H = 8.94$ .

II. 0.1441 „ 0.3334 „ „ 0.1155 „  $C = 63.10$ ;  $H = 8.90$ .

$C(CH_3)_2 \cdot C(CH_3) \cdot COOH$  requires  $C = 63.15$ ;  $H = 8.77$  per cent.

*Trimethylacrylic acid*, when moderately rapidly heated in a capillary tube, softens at  $67^\circ$ , and melts at  $70\text{--}71^\circ$ . It is readily soluble in hot light petroleum, benzene, alcohol, ether, and chloroform, sparingly in hot water. The hot concentrated aqueous solution becomes milky on standing, and then gradually deposits crystals, but, on slowly cooling a hot dilute aqueous solution, the acid crystallises well in long, colourless needles.



The solution of the pure acid in sodium carbonate decolorises potassium permanganate, but not nearly so rapidly as many other unsaturated acids.

*Trimethylacrylic Anilide*,  $C(CH_3)_2 \cdot C(CH_3) \cdot CO \cdot NH \cdot C_6H_5$ .

This substance was prepared in the following way. Pure trimethylacrylic acid was mixed with excess of freshly distilled phosphorus trichloride, and, as very little action appeared to take place in the cold, the whole was heated on the water bath for about 15 minutes. On fractionating the product, a considerable quantity distilled at  $145-150^\circ$ , and evidently consisted of trimethylacrylic chloride,  $C(CH_3)_2 \cdot C(CH_3) \cdot CO \cdot Cl$ . This was dissolved in pure dry ether, mixed with excess of aniline, and, as soon as the very vigorous action had subsided, the whole was treated with water and extracted with ether. The ethereal solution was washed first with dilute hydrochloric acid and then with sodium carbonate, dried over anhydrous potassium carbonate, and the ether distilled off, when a syrupy residue was obtained, which, on standing, gradually solidified.

In order to purify this crude substance, it was ground up with cold light petroleum, collected on a filter, and recrystallised twice from boiling light petroleum (b. p.  $70-80^\circ$ ).

0.2133 gave 14.0 c.c. moist nitrogen at  $20^\circ$  and 765 mm.  $N = 7.55$ .

$C_{12}H_{15}NO$  requires  $N = 7.41$  per cent.

*Trimethylacrylic anilide* melts at  $93-94^\circ$ , and crystallises from hot light petroleum in beautiful, glistening plates. It is readily soluble in alcohol, ether, and benzene, sparingly in light petroleum, and almost insoluble in water.

*Dibromotrimethylpropionic acid*,  $CBr(CH_3)_2 \cdot CBr(CH_3) \cdot COOH$ .

A solution of trimethylacrylic acid in chloroform decolorises bromine rapidly, and if, after the addition of the calculated quantity of bromine, the liquid is allowed to evaporate spontaneously, a semi-solid residue is obtained, consisting of impure dibromotrimethylpropionic acid. The crude product was left in contact with porous porcelain for some days until the oily impurities had been entirely absorbed, and the solid residue purified by recrystallisation from light petroleum (b. p.  $100-105^\circ$ ).

0.1547 gram substance, heated with nitric acid and nitrate of silver at  $180^\circ$ , gave 0.2128 gram  $AgBr$ ;  $Br = 58.54$ .

$C_6H_{10}Br_2O_2$  requires  $Br = 58.40$  per cent.

*Dibromotrimethylpropionic acid* is very sparingly soluble in cold light petroleum, but dissolves fairly readily on warming, and separates

again, on standing, as a heavy, white, crystalline powder. When heated in a capillary tube, it sinters at  $185^{\circ}$ , and melts at  $190$ — $191^{\circ}$  with rapid evolution of gas.

*$\beta$ -Bromotrimethylpropionic acid*,  $\text{CBr}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$ .

In order to prepare this substance, finely powdered trimethylacrylic acid (1 gram) was mixed in a test tube with 5 c.c. of fuming hydrobromic acid saturated at  $0^{\circ}$ . On gently warming the mixture, the acid completely dissolved, but very soon an oily layer formed on the surface. After standing for 10 minutes, an equal volume of water was added, and the crystals which separated were collected, well washed with water, drained on a porous plate, and dried over sulphuric acid in a vacuum. As the substance could not be satisfactorily recrystallised, the colourless, crystalline mass obtained in this way was directly analysed.

0.1431 gram substance, heated at  $200^{\circ}$  with nitric acid and nitrate of silver, gave 0.1375 gram  $\text{AgBr}$ .  $\text{Br} = 40.92$ .

$\text{C}_6\text{H}_{11}\text{BrO}_2$  requires  $\text{Br} = 41.02$  per cent.

*$\beta$ -Bromotrimethylpropionic acid*, when heated in a capillary tube, softens at  $83^{\circ}$  and melts at about  $87$ — $88^{\circ}$ . It is readily soluble in most organic solvents, but practically insoluble in water. When boiled with water, it is rapidly decomposed with separation of hydrogen bromide.

*$\beta$ -Iodotrimethylpropionic acid*,  $\text{CI}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$ .

Trimethylacrylic acid dissolves readily in fuming hydriodic acid (sp. gr. 1.96) in the cold, and, on standing, the solution gradually deposits beautiful crystals of  *$\beta$ -iodotrimethylpropionic acid*. After diluting with water, the crystals were collected, washed well with water, and dried on a piece of porous porcelain over sulphuric acid in a vacuum. The analysis of the glistening, crystalline mass thus obtained gave the following results.

0.1439 gram substance, heated with silver nitrate and nitric acid at  $170^{\circ}$ , gave 0.1390 gram  $\text{AgI}$ .  $\text{I} = 52.23$ .

$\text{C}_6\text{H}_{11}\text{IO}_2$  requires  $\text{I} = 52.48$  per cent.

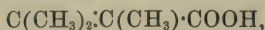
*$\beta$ -Iodotrimethylpropionic acid* melts at  $80$ — $82^{\circ}$ , and, when heated in a test tube, it rapidly decomposes with separation of iodine and evolution of hydrogen iodide; it also decomposes on exposure to strong sunlight, with separation of iodine. It is readily soluble in alcohol, light petroleum, chloroform, and ether, but almost insoluble in cold water. Cold concentrated nitric acid decomposes it instantly, with separation of crystals of iodine.

*Condensation of Acetone with Ethylic  $\alpha$ -Bromopropionate. Formation of Ethylic  $\beta$ -Hydroxy- $\alpha\beta\beta$ -trimethylpropionate,*

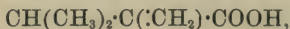


[With J. F. THORPE.]

This condensation was studied, as explained in the introduction, with the object of synthesising trimethylacrylic acid,



and its derivatives by a method which could leave no doubt as to their constitution, and the results obtained served to prove conclusively that the solid acid (melting at  $71^\circ$ ) produced, as already described, by the hydrolysis of ethylic bromotrimethylpropionate, was in fact this acid, and not isopropylacrylic acid,



as was at one time thought to be the case.

The first step was to prepare ethylic  $\beta$ -hydroxy- $\alpha\beta\beta$ -trimethylpropionate, and this is accomplished as follows.

Acetone (90 grams) is mixed with ethylic  $\alpha$ -bromopropionate (182 grams), and the mixture poured on to an excess of dry and carefully cleaned zinc in a moderately large flask connected with a reflux apparatus. The zinc, which should be in the form of turnings, must be quite free from oil, and it is also essential that it should be quite dry. We found it necessary to wash it several times with hot caustic soda, then with dilute acid to remove any oxide, and finally to wash it well with water and dry it with alcohol and ether. Experiments conducted with zinc which had not been treated in this way were always unsuccessful. The flask containing a little of the zinc in contact with the mixture is now gently warmed on the water bath, when, as soon as the temperature has risen to about  $50^\circ$ , the action usually commences and continues very energetically; the flask is removed from the water bath if necessary, but as a rule the excess of acetone employed serves to prevent the temperature from rising too high. When the reaction has subsided, if it is found that nearly all the zinc has disappeared, more is added, and the whole ultimately heated on the water bath for about 2—3 hours; at the end of this time the contents of the flask will have become quite thick and slightly coloured.

The syrupy liquid is poured off as far as possible from the unchanged zinc, and mixed with water; this causes the mass to become nearly solid, owing to the separation of a white zinc compound, which, however, disappears on adding dilute sulphuric acid and shaking vigorously. The oil which separates is extracted by means of ether,



the ethereal solution is washed three times with dilute sulphuric acid in order to remove the last traces of zinc, dried over calcium chloride, the ether distilled off, and the residual oil purified by careful fractionation under reduced pressure (30 mm.).

A considerable portion of the product distils below  $100^{\circ}$ , and appears to consist essentially of ethylic propionate and ethylic acrylate, the former produced by the reduction of, and the latter by the elimination of hydrogen bromide from, the ethylic  $\alpha$ -bromopropionate employed in this synthesis. About 50 per cent. of the whole distils at  $105^{\circ}$  (30 mm.) as a moderately thick, colourless oil of very faint odour, which after redistillation gave the following results on analysis.

- I. 0.1186 gave 0.2616  $\text{CO}_2$  and 0.1076  $\text{H}_2\text{O}$ . C = 60.16; H = 10.08.  
 II. 0.1309 „ 0.2872 „ „ 0.1198 „ C = 59.82; H = 10.16.  
 $\text{C}_8\text{H}_{16}\text{O}_3$  requires C = 60.00; H = 10.00 per cent.

This substance consists, therefore, of pure *ethylic  $\beta$ -hydroxy- $\alpha\beta\beta$ -trimethylpropionate*.

*$\beta$ -Hydroxy- $\alpha\beta\beta$ -trimethylpropionic acid*,  $\text{OH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ .  
 [With J. F. THORPE.]

In order to prepare this acid, the corresponding ethereal salt just described was mixed with excess of a solution of potash ( $1\frac{1}{2}$  mols.) in pure alcohol, and heated on the water bath for two hours. Water was then added, the solution evaporated until quite free from alcohol, acidified, and extracted several times with pure ether, the extraction being much facilitated by saturating the solution with ammonium sulphate. The ethereal solution was carefully dried over calcium chloride, filtered, evaporated, and the thick, syrupy residue purified by distillation in small quantities under reduced pressure; almost the whole passed over at  $160^{\circ}$  (35 mm.) as a very thick, viscid, colourless oil which, on analysis, gave the following numbers.

- I. 0.1888 gave 0.3814  $\text{CO}_2$  and 0.1592  $\text{H}_2\text{O}$ . C = 55.08; H = 9.37.  
 II. 0.1318 „ 0.2650 „ „ 0.1106 „ C = 54.83; H = 9.32.  
 $\text{C}_6\text{H}_{12}\text{O}_3$  requires C = 54.54; H = 9.09 per cent.

*$\beta$ -Hydroxy- $\alpha\beta\beta$ -trimethylpropionic acid* is a very thick syrup, which even on long standing does not show any signs of crystallising. It is readily soluble in water, the solution having a strongly acid reaction. When distilled in large quantities (100 grams), it decomposes with elimination of water and formation of trimethylacrylic acid.

The dissociation constant for the electrical conductivity of this acid at different concentrations was determined by Dr. Ewan, who found  $K = 0.00333$ .



*β-Bromo-αβ-trimethylpropionic acid*,  $\text{CBr}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$ .  
[With J. F. THORPE.]

This substance, which is identical with the bromo-acid obtained by the addition of hydrogen bromide to trimethylacrylic acid (p. 1481), is obtained by dissolving *β*-hydroxytrimethylpropionic acid in fuming hydrobromic acid (saturated at  $-10^\circ$ ). The mixture becomes warm, and, on standing, the bromo-acid rapidly separates in lustrous plates, which, after washing with water and drying on a porous plate over sulphuric acid in a vacuum, melt at  $86-88^\circ$ .

0.2012 gram substance, heated at  $180^\circ$  with silver nitrate and nitric acid, gave 0.1919 gram AgBr.  $\text{Br} = 40.98$  per cent.

$\text{C}_6\text{H}_{11}\text{BrO}_2$  requires  $\text{Br} = 41.02$  per cent.

*Ethyl β-bromo-αβ-trimethylpropionate*,  
 $\text{C}(\text{CH}_3)_2\text{Br} \cdot \text{CH}(\text{CH}_3) \cdot \text{COOC}_2\text{H}_5$ .—[With J. F. THORPE.]

In order to prepare this compound for some synthetical experiments described below, the etherification of the corresponding acid by means of alcohol and sulphuric acid, and by saturating the solution of the acid in alcohol with hydrogen chloride was tried, but with very unsatisfactory results. Ultimately, however, the ethereal salt was prepared in considerable quantity, with ease, in the following way.

The pure dry bromo-acid (10 grams) was mixed with phosphorus pentachloride (12 grams) and allowed to stand until the somewhat energetic action had subsided: the whole was then heated on the water bath for 15–20 minutes, and the product poured into absolute alcohol and allowed to stand over night. On adding water, a heavy, brownish oil was precipitated; this was extracted with ether, the ethereal solution well washed with water and dilute sodium carbonate, dried over calcium chloride, and the ether distilled off. The residual, somewhat brownish oil did not appear to distil without decomposition; but after standing over sulphuric acid in a vacuum for a few days, it gave the following results on analysis, showing it to consist of the nearly pure ethereal salt.

0.2103 gave 0.1760 AgBr.  $\text{Br} = 35.96$ .

$\text{C}_8\text{H}_{15}\text{O}_2\text{Br}$  requires  $\text{Br} = 36.16$  per cent.

Many experiments with this substance were made with the object of synthesising *αββ*-trimethylglutaric acid so as to be able to compare it with the acid Balbiano obtained by the oxidation of camphoric acid with cold potassium permanganate (*Ber.*, 1895, **28**, 1507); the method of procedure will be well understood from the following equations.

- I.  $(\text{COOC}_2\text{H}_5)_2\text{CHNa} + \text{CBr}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5 =$   
 $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5 + \text{NaBr}.$
- II.  $(\text{COOH})_2\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH} =$   
 $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH} + \text{CO}_2.$

The action of the brom-etheral salt on the sodium derivative of ethylic malonate was tried under various conditions in alcoholic and xylene solution, but only very small quantities of a high boiling condensation product were formed in any case, and similar results were obtained when ethylic cyanoacetate was employed. Apparently in all these experiments the bromo-etheral salt is to some extent decomposed with elimination of hydrogen bromide and formation of ethylic trimethylacrylate; the reaction, however, is evidently a complicated one, as is shown by the fact that in all the above experiments the product was found to contain considerable quantities of ethylic ethane-tetracarboxylate  $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2.$

*$\beta$ -Iodo- $\alpha\beta\beta$ -trimethylpropionic acid*,  $\text{C}(\text{CH}_3)_2\text{I}\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}.$

$\beta$ -Hydroxytrimethylpropionic acid dissolves readily in fuming hydriodic acid, and, on standing, crystals of the above substance separate rapidly. The crystals were collected, washed with water, dried on a porous plate over sulphuric acid in the dark, and analysed.

0.1296 gave 0.1252 AgI.  $\text{I} = 52.39.$

$\text{C}_6\text{H}_{11}\text{I}\cdot\text{O}_2$  requires  $\text{I} = 52.48$  per cent.

This acid melts at  $80^\circ$  and is identical with the compound obtained by the addition of hydrogen iodide to trimethylacrylic acid (p. 1481). When it is treated with phosphorous pentachloride, and the product is poured into alcohol under exactly the same conditions as described in the case of the corresponding bromo-acid, it yields a heavy ethereal salt, which cannot be distilled without decomposition; it was not analysed.

*Trimethylacrylic acid*,  $\text{C}(\text{CH}_3)_2\cdot\text{C}(\text{CH}_3)\cdot\text{COOH}.$ —[With J. F. THORPE.]

This acid is produced when alcoholic potash, or weak alkalis, such as the sodium derivative of ethylic malonate, act on ethylic  $\beta$ -bromo-trimethylpropionate. It was first obtained from this ethereal salt in the following manner.

The low boiling fractions from the product of the action of the bromo-etheral salt on the sodium derivative of ethylic malonate (see above) were hydrolysed by boiling for three hours with an excess of alcoholic potash. The alkaline solution was then evaporated with water until free from alcohol, acidified, and extracted with ether;

the ethereal solution after being dried over calcium chloride was evaporated, and the residual oil fractionated under reduced pressure. The fraction boiling at 135—137° (50 mm.) solidified on cooling, and the crystals, after being drained on a porous plate and crystallised from water, consisted of pure trimethylacrylic acid melting at 70—71°.

0.2201 gave 0.5085 CO<sub>2</sub> and 0.1737 H<sub>2</sub>O. C = 63.00; H = 8.79.

C<sub>6</sub>H<sub>10</sub>O<sub>2</sub> requires C = 63.15; H = 8.77 per cent.

The silver salt, C<sub>6</sub>H<sub>9</sub>AgO<sub>2</sub>, was obtained as a white precipitate sparingly soluble in water, on adding silver nitrate to the neutral solution of the ammonium salt.

0.2002, on ignition, gave 0.0970 Ag. Ag = 48.73.

C<sub>6</sub>H<sub>9</sub>AgO<sub>2</sub> requires Ag = 48.77 per cent.

After these experiments had been carried out, it was found that the same acid was obtained by the hydrolysis of ethylic β-bromotrimethylpropionate with alcoholic potash; and the acid obtained in both cases was found to be identical with the trimethylacrylic acid obtained by the hydrolysis of ethylic α-bromotrimethylpropionate (p. 1479). As this was an important point, a sample of the trimethylacrylic acid obtained from the β-brom-ethereal salt by means of alcoholic potash was dissolved in chloroform and treated with bromine under the conditions described on p. 1480.

The resulting dibromide melted at 190—191°, and was identical in all respects with the dibromotrimethylpropionic acid previously obtained.

0.1398 gave 0.191 AgBr. Br = 58.10.

C<sub>6</sub>H<sub>10</sub>BrO<sub>2</sub> requires Br = 58.40 per cent.

*α-Hydroxytrimethylpropionic acid*, CH(CH<sub>3</sub>)<sub>2</sub>·C(OH)(CH<sub>3</sub>)·COOH.

In distilling the crude acid obtained by the hydrolysis of ethylic α-bromotrimethylpropionate with alcoholic potash, a mixture of isopropylacrylic acid and trimethylacrylic acid at first passed over as explained on p. 1479; the thermometer then rose rapidly, and a thick colourless oil distilled over which after standing for some months deposited prismatic crystals. These were collected, drained on a porous plate, and purified by recrystallisation from light petroleum (b. p. 60—80°), when they were obtained in the form of glistening, colourless needles which, on analysis, gave the following numbers.

I. 0.1931 gave 0.3874 CO<sub>2</sub> and 0.1598 H<sub>2</sub>O. C = 54.73; H = 9.20.

II. 0.1601 „ 0.3225 „ „ 0.1305 „ C = 54.90; H = 9.06.

III. 0.1765 „ 0.3511 „ „ 0.1451 „ C = 54.25; H = 9.12.

C<sub>6</sub>H<sub>12</sub>O<sub>3</sub> requires = 54.54; H = 9.09 per cent.



*α-Hydroxytrimethylpropionic acid* melts at 75—77°, but not very sharply. It is very readily soluble in water, the solution possessing a very strong acid reaction. It is readily soluble in alcohol, ether, or chloroform, moderately in benzene, and sparingly in cold, light petroleum. When thrown on to the surface of water, the crystals of the acid rotate in a very vigorous manner and dissolve rapidly.

The dissociation constant for the electrical conductivity of this acid at different concentrations at 25°, was found by Dr. Ewan to be  $K = 0.01135$ . It is remarkable that this value should be so high in comparison with the constant ( $K = 0.00333$ ) for the corresponding *β*-hydroxy-acid (p. 1483).

*Salts of α-Hydroxytrimethylpropionic acid.*

The *silver salt*,  $C_6H_{11}AgO_3$ , obtained as a white precipitate on the addition of silver nitrate to a strong neutral solution of the ammonium salt of the acid, is sparingly soluble in cold water, but dissolves readily on boiling, and the hot solution on cooling deposits the salt in a beautifully crystalline condition.

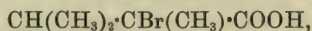
0.2445 gave 0.1105 Ag.  $Ag = 45.19$ .

$C_6H_{11}AgO_3$  requires  $Ag = 45.18$  per cent.

This silver salt is not readily acted on by light, and may be dried at 100° without decomposition; its solution in dilute ammonia is only very slowly decomposed on boiling.

A neutral solution of the ammonium salt of the acid shows the following behaviour with reagents. *Copper acetate* no precipitate in the cold, but, on boiling, a pale blue crystalline copper salt separates; this gradually decomposes on prolonged boiling, especially if a little alkali be present, and cuprous oxide is precipitated. *Barium* and *calcium chlorides*, and *lead acetate* give no precipitate.

*Action of Hydrobromic acid and Hydriodic acid on α-Hydroxytrimethylpropionic acid.*—This reaction was investigated in the hope of easily obtaining *α*-bromotrimethylpropionic acid,



and *α*-iodotrimethylpropionic acid,  $CH(CH_3)_2 \cdot CI(CH_3) \cdot COOH$ , for comparison with the corresponding *β*-halogen derivatives which had been prepared from *β*-hydroxytrimethylpropionic acid and trimethylacrylic acid by the methods described on pp. 1484–1485. It was found that *β*-hydroxytrimethylpropionic acid reacts very readily with concentrated hydrobromic and hydriodic acids in the cold, forming the corresponding *β*-halogen derivatives, but the behaviour of the corresponding *α*-hydroxy-acid is very different in this respect. The latter dissolves very readily in the concentrated haloïd acids, but no action

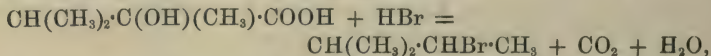


appears to take place, as was shown by the fact that, after remaining at the ordinary temperature for 12 hours, no crystals had separated, and a drop of the liquid dissolved in water formed a clear solution. The solutions were then sealed up in tubes and heated in boiling water, but even then the action seemed to take place very slowly, the liquids only becoming turbid after two hours' boiling. After eight hours, the tubes were allowed to cool, when, on opening them, a considerable pressure was noticed, which was found to be due to carbon dioxide, and, on pouring the contents of the tubes into water, a heavy oil was precipitated in each case. This was extracted with ether, the ethereal solution washed well with water and dilute sodium carbonate (and, in the case of the hydriodic acid experiment, also with sodium thiosulphate to remove iodine), evaporated and the nearly colourless, oily residues fractionated. After twice fractionating, in the case of the hydrobromic acid experiment a small quantity of a heavy oil was obtained, which boiled at 115—120°, and on analysis gave the following result.

0.1420 gram heated with silver nitrate and fuming nitric acid at 200° for 4 hours gave 0.1711 gram AgBr. Br = 51.10 per cent.

$C_5H_{11}Br$  requires Br = 52.98 per cent.

Although, owing to the difficulty of purifying the small amount of material at my disposal, this analysis does not agree well with the formula  $C_5H_{11}Br$ , it seems probable that this bromide is identical with methylisopropylcarbonyl bromide,  $CH(CH_3)_2 \cdot CHBr \cdot CH_3$ , which Wischnegradsky (*Annalen*, 1878, **190**, 357) obtained by the action of hydrogen bromide on isopropylethylene,  $CH(CH_3)_2 \cdot CH \cdot CH_2$ , and which boils at 114—116°. The formation of this substance would be readily explained by the following equation:



but it is certainly remarkable that an  $\alpha$ -bromo-fatty acid, which one would expect to be formed in the first instance, should lose carbon dioxide in this way, as this is a decomposition usually only shown by  $\beta$ -bromo-derivatives. The oil obtained from the hydriodic acid experiment distilled roughly at 125—130°, and is possibly methylisopropylcarbonyl iodide,  $CH(CH_3)_2 \cdot CHI \cdot CH_3$ , which, according to Wischnegradsky (*Annalen*, 1878, **190**, 337), boils at 127—128°; it was not analysed.

*Preparation of the mixed Ethereal Salts of Isopropylacrylic acid and of Trimethylacrylic acid.*

The greater portion of these mixed ethereal salts used in the first experiments in this research was prepared by the etherification of

the mixture of isopropylacrylic and trimethylacrylic acids obtained by the hydrolysis of ethylic  $\alpha$ -bromotrimethylpropionate by means of alcoholic potash, as explained on p. 1462 (Method I). The action of quinoline on the brominated ethereal salt (Method II) was not investigated until most of the experiments described in this paper had been completed.

*Method I.*—The mixed ethereal salts were prepared by dissolving the mixed acids (1 vol.) in absolute alcohol (3 vols.), and adding concentrated sulphuric acid (1 vol.). After standing overnight, water was added, the oily layer extracted with ether, the ethereal solution washed with sodium carbonate solution, dried over anhydrous potassium carbonate, evaporated, and the residual crude ethereal salt purified by repeated fractional distillation. Although this ethereal salt has been prepared in large quantities (500 grams) on several occasions, it has always been found very difficult to obtain a product of anything like constant boiling point, and, for this reason, in the experiments described in this paper the fraction 162—175° was usually employed. It is, of course, possible that the ethereal salts of the two acrylic acids may boil at different temperatures, but it is more probable that the product contains small quantities of ethylic  $\alpha$ -hydroxytrimethylpropionate, produced by the action of the sulphuric acid on the unsaturated acids during the process of etherification, and this is borne out by the results obtained by the analysis of different fractions, which were always too low. I (b. p. 163—165°); II (b. p. 166—168°); III (b. p. 168—172°).

I.	0.1240	gave	0.3020	CO <sub>2</sub>	and	0.1094	H <sub>2</sub> O.	C = 66.43;	H = 9.80.
II.	0.1561	„	0.3758	„	„	0.1360	„	C = 65.66;	H = 9.67.
III.	0.1404	„	0.3379	„	„	0.1218	„	C = 65.64;	H = 9.64.
C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> requires C = 67.60; H = 9.86 per cent.									

The presence of the impurity, whatever it may be, in the fraction 162—175°, does not interfere with the experiment for which it was employed (condensation with ethylic malonate), except, of course, in so far as it may affect the yield of the condensation product.

*Method II.*—A mixture of ethylic  $\alpha$ -bromotrimethylpropionate (100 grams) and quinoline (200 grams) was heated in a metal bath in a flask connected with a reflux apparatus, the temperature of the mixture being observed by placing a thermometer in the liquid.

When the temperature had risen to 175—180°, the reaction set in, and on removing the flame the liquid boiled, though not violently, for some minutes, the thermometer rising to about 195°. As soon as the action had subsided, the mixture was heated to boiling for 10 minutes, the well-cooled, dark reddish-brown product poured into an excess of dilute hydrochloric acid, and the oily layer extracted twice with ether.

After well washing with dilute hydrochloric acid and drying over calcium chloride, the ether was distilled off and the residual oil purified by repeated fractionation, when the greater part was found to distil between  $162^{\circ}$  and  $175^{\circ}$ , the quantity obtained being about 60—70 per cent. of the theoretical yield. This fraction, on analysis, gave only approximately correct results.

0.1364 gave 0.3344  $\text{CO}_2$  and 0.1209  $\text{H}_2\text{O}$ .  $\text{C} = 66.86$ ;  $\text{H} = 9.86$ .

$\text{C}_8\text{H}_{14}\text{O}_2$  requires  $\text{C} = 67.60$ ;  $\text{H} = 9.85$  per cent.

In order to prove that this ethereal salt was a mixture of the ethereal salts of isopropylacrylic and trimethylacrylic acids, it was hydrolysed by boiling with alcoholic potash in the usual manner. The acid obtained distilled at  $148$ — $150^{\circ}$  (100 mm.), and, on standing in a freezing mixture, deposited crystals of trimethylacrylic acid. The filtrate from these crystals did not solidify on cooling, and was proved to contain isopropylacrylic acid.

Apparently, then, the elimination of hydrogen bromide from ethylic  $\alpha$ -bromotrimethylpropionate proceeds in the same way, whether alcoholic potash or quinoline be employed, a mixture of isopropylacrylic acid and trimethylacrylic acid, or their ethereal salts, being formed in both cases.

*Condensation of Ethylic Isopropylacrylate with the Sodium Derivative of Ethylic Malonate. Formation of Ethylic  $\alpha$ -Isopropylpropane- $\alpha\alpha_1\alpha_1$ -tricarboxylate,  $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_3\text{H}_7)\cdot\text{COOC}_2\text{H}_5$ .*

The study of the reaction which takes place when the mixed ethereal salts of isopropylacrylic acid and trimethylacrylic acid are treated with the sodium compound of ethylic malonate has been made the subject of a very large number of experiments, carried out under very varying conditions, a description of which would occupy too much space to be given here. The product formed in every case was ethylic isopropylpropanetricarboxylate produced by the condensation of ethylic isopropylacrylate with ethylic malonate, the ethylic trimethylacrylate, as explained in the introduction, apparently taking no part in the reaction.

The yield of condensation product was found to be much influenced by the purity of the unsaturated ethereal salts; thus, for instance, when the mixture of ethylic isopropylacrylate and ethylic trimethylacrylate had been fractionated four times with a column, and the fraction  $162$ — $175^{\circ}$  employed, a yield of 20 per cent. of the theoretical was obtained, whereas, in one case, where the ethereal salts had been fractionated only once, and the fraction  $160$ — $177^{\circ}$  used for the condensation the yield was only 8 per cent.



Ultimately, the condensation was usually carried out in the following way.

In a flask connected with a reflux condenser, sodium (46 grams) was dissolved in absolute alcohol (500 grams), and then, while still slightly warm, first ethylic malonate (320 grams) and then the mixture (164 grams) of the ethereal salts of isopropylacrylic acid and trimethylacrylic acid were added; the product was subsequently heated for one day at  $60^{\circ}$ , and then for two days on a water bath. The opaque, somewhat dark-coloured product was mixed with twice its volume of water, acidified with hydrochloric acid, and extracted three times with ether; the ethereal solution was washed well with water and dilute sodium carbonate, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure. The yield of crude product and the weight of the various fractions obtained varied very much, without any apparent cause; the following result was obtained in one case, where the products from an experiment carried out with the quantities given above were weighed.

The yield of crude product was 244 grams, and this on fractionation under reduced pressure (80 mm.) gave the following fractions:

Below $160^{\circ}$	= 98	grams.
160—220	= 16	„
220—235	= 92	„
Residue	= 16	„

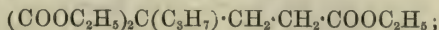
the fraction below  $160^{\circ}$  consists principally of ethylic trimethylacrylate, unchanged ethylic isopropylacrylate, and some unchanged ethylic malonate.\* The fraction  $220-235^{\circ}$  is nearly pure ethylic isopropylpropanetricarboxylate.

The latter, on refractionation, boiled almost constantly at  $208-210$  (45 mm.), and gave the following results† on analysis.

I.	0.1610	gave	0.3486	$\text{CO}_2$	and	0.1247	$\text{H}_2\text{O}$ .	C = 59.04; H = 8.60.
II.	0.1392	„	0.2998	„	„	0.1075	„	C = 58.74; H = 8.50.
III.	0.1288	„	0.2796	„	„	0.1000	„	C = 59.20; H = 8.63.

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires C = 59.60; H = 8.61 per cent.

*Ethylic isopropylpropanetricarboxylate* is a thick, perfectly colourless oil which boils at  $208-210^{\circ}$  under a pressure of 45 mm.; it is isomeric with the ethereal salt obtained by treating the sodium compound of ethylic isopropylmalonate with ethylic  $\beta$ -iodopropionate (see p. 1507), and which has the formula



\* A large amount of the ethylic malonate employed in the above preparation is hydrolysed during the prolonged heating.

† These analyses were carried out with the products obtained from three different preparations.



both ethereal salts are very similar in properties, and boil practically at the same temperature, and both, on hydrolysis and subsequent elimination of carbon dioxide, yield the same isopropylglutaric acid.

*$\alpha$ -Isopropylpropane- $\alpha\alpha_1\alpha_1$ -tricarboxylic acid,*  
 $(\text{COOH})_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{C}_3\text{H}_7)\cdot\text{COOH}.$

The ethylic isopropylpropanetricarboxylate, prepared as described in the last paragraph, although it gives good results on analysis, is not quite pure, but contains traces of other ethereal salts, and on this account, for a considerable time, it was found impossible to obtain crystalline isopropylglutaric acid from it by hydrolysis and subsequent elimination of carbon dioxide. The oily acid obtained in this way refused to crystallise after standing for a month in a cool place, and even after converting it into its anhydride, fractionating this and regenerating the acid, the product did not crystallise. Ultimately it was discovered that pure isopropylpropanetricarboxylic acid may be readily purified by the following method, and that this pure acid, on subsequent heating at  $180^\circ$ , yields pure isopropylglutaric acid which crystallises quite readily.

Ethylic isopropylpropanetricarboxylate (40 grams) is hydrolysed by boiling for one hour with pure potash (50 grams) dissolved in methylic alcohol; the clear liquid is then mixed with water, and evaporated on a water bath, with the addition from time to time of small quantities of water, until every trace of methylic alcohol has been removed. The concentrated solution of the potassium salt, after acidifying, is extracted 10 times with pure ether (free from alcohol), the ether evaporated, the oily residue dissolved in twice its volume of water, and the solution saturated with hydrogen chloride, the temperature being kept below  $40^\circ$  by cooling with ice-cold water.

During this operation, crystals begin to separate, and, on standing for two days, the bulk of the tribasic acid separates in crystalline crusts; these are collected on the pump, washed with concentrated hydrochloric acid, and purified by solution in water and saturation with hydrogen chloride as before.

I. 0.1130 gave 0.2045  $\text{CO}_2$  and 0.0661  $\text{H}_2\text{O}$ . C = 49.36; H = 6.50.

II. 0.1243 „ 0.2235 „ „ 0.0735 „ C = 49.04; H = 6.57.

$\text{C}_9\text{H}_{14}\text{O}_6$  requires C = 49.54; H = 6.42 per cent.

*Isopropylpropanetricarboxylic acid*, when moderately rapidly heated in a capillary tube, melts at  $165^\circ$  with rapid decomposition, due to evolution of carbon dioxide and formation of isopropylglutaric acid, but if slowly heated, the decomposition takes place at a lower temperature, generally about  $158^\circ$ . It is very readily soluble in water,

the solution possessing a very strong acid reaction, but it is only sparingly soluble in concentrated hydrochloric acid; it dissolves also readily in alcohol, and moderately so in ether.

*Salts of Isopropylpropanetricarboxylic acid.*—The *silver salt* was prepared by adding silver nitrate to a fairly concentrated warm solution of the ammonium salt. It is a white, amorphous precipitate, which, after washing well with warm water, and drying first on a porous plate over sulphuric acid in a vacuum, and then at 100°, gave the following result on analysis.

0.3464, on ignition, gave 0.2064 Ag. Ag = 59.58.

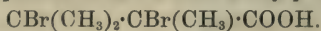
$C_9H_{11}Ag_3O_6$  requires Ag = 60.11 per cent.

A neutral solution of the ammonium salt gives no precipitate with *calcium chloride* or *copper acetate*, but a white, gelatinous precipitate is formed with *lead acetate*. On the addition of *barium chloride*, no precipitate is produced at first, but on standing, or more rapidly on warming, an insoluble crystalline barium salt separates.

From the experiments already described it seemed probable, as stated in the introduction, that when a mixture of ethylic isopropylacrylate and ethylic trimethylacrylate is digested with the sodium derivative of ethylic malonate, that the former alone undergoes condensation, the latter remaining unchanged; in order to determine, therefore, whether this was really the case the following experiments were made.

*Experiment I.*—The oil boiling below 160° (80 mm.), obtained in fractionating the product of the action of the mixed ethereal salts on ethylic malonate, as described on page 1491, was collected from several operations, carefully fractionated with a column, and the fraction 160—175° digested with a large excess of the sodium derivative of ethylic malonate in alcoholic solution, for about three days. The product was isolated as before, and, on fractionation, yielded a small quantity of ethylic isopropylpropanetricarboxylate, showing that small quantities of ethylic isopropylacrylate were present in the ethereal salt employed. The large quantity of oil of low boiling point, which was obtained during the fractionation, was again treated with ethylic malonate as before, and yielded now only traces of ethylic isopropylpropanetricarboxylate; it was very carefully fractionated, and the fraction boiling at 160—175° hydrolysed by boiling with alcoholic potash, and the acid obtained fractionated under reduced pressure, the fraction 135—142° (90 mm.) being collected separately. Owing to the mildness of the summer weather, this oil, which should contain the recovered trimethylacrylic acid, showed no signs of crystallising; it was, therefore, dissolved in chloroform,

and titrated with bromine until the colour remained permanent, when about 80 per cent. of the theoretical quantity of bromine was absorbed, showing that this crude acid must contain a small quantity of some saturated acid as impurity. On allowing the chloroform to evaporate spontaneously, crystals gradually separated from the oily residue; these were collected, spread on a porous plate, and recrystallised from light petroleum; the substance then melted at  $185-190^{\circ}$ , and had all the properties of dibromotrimethylpropionic acid,

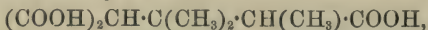


0.1391 gave 0.1906 AgBr.  $\text{Br} = 58.58$ .

$\text{C}_6\text{H}_{10}\text{Br}_2\text{O}_2$  requires  $\text{Br} = 58.40$  per cent.

The formation of this substance shows that when the mixture of ethylic isopropylacrylate and ethylic trimethylacrylate is digested with the sodium derivative of ethylic malonate, *some* of the latter, at all events, remains unattacked, even when the operation is repeated three times.

*Experiment II.*—Attempts were now made to determine whether any of the ethylic trimethylacrylate had taken part in the reaction, in which case ethylic trimethylpropanetricarboxylate must have been formed, and, on hydrolysing the product of the condensation, trimethylpropanetricarboxylic acid,



would be obtained mixed with large quantities of isopropylpropanetricarboxylic acid.

If this were the case, the former acid must be contained in the hydrochloric acid mother liquors, from which the latter acid had crystallised out as explained on p. 1492. These mother liquors were collected, extracted about 20 times with pure ether, the ether evaporated, and the residual oily acid, dissolved in a little water, was saturated with hydrogen chloride, the whole being well cooled during the operation.

After standing for a fortnight, the crystals of isopropylpropanetricarboxylic acid which had separated were removed by filtration through a platinum cone, the filtrate again extracted with ether, and the treatment with hydrogen chloride repeated. Lastly, the small quantity of acid which did not crystallise was heated at  $180^{\circ}$ , and the residue etherified by treatment with alcohol and sulphuric acid, when an oily, ethereal salt was obtained which distilled, for the most part, at  $170-172^{\circ}$  (90 mm.).

As the acid obtained from this on hydrolysis did not solidify, it was converted into the anhydride by boiling with acetic anhydride, and the product (3 grams) fractionated, the fraction  $170-175^{\circ}$  (30 mm.) being reconverted into the acid; the oily acid was then



dissolved in a little water, and the solution saturated with hydrogen chloride. On standing, about 1 gram of a crystalline acid separated which melted at 90—93°, and consisted evidently of isopropylglutaric acid, since it gave an anhydride melting at 53°, and an anilic acid melting at 156—158°.

As far as can be judged from these experiments, it appears that ethylic trimethylacrylate is not capable of condensing with ethylic malonate, and I hope to prove this definitely by experiments with pure ethylic trimethylacrylate.

*Isopropylglutaric acid*,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

In order to prepare this acid, *pure* isopropylpropanetricarboxylic acid is heated in an oil bath at 200° until the evolution of carbon dioxide has entirely ceased; the residue is dissolved in boiling water, and the solution, after cooling, saturated with hydrogen chloride. After standing overnight, the colourless crystals which separate are collected on a platinum cone by the aid of the pump, washed with concentrated hydrochloric acid, and recrystallised by dissolving them in a little water and saturating with hydrogen chloride as before.

The analysis of this acid gave the following results.

- I. 0.1485 gave 0.2970  $\text{CO}_2$  and 0.1073  $\text{H}_2\text{O}$ . C = 54.54; H = 8.03.  
 II. 0.1188 „ 0.2388 „ „ 0.0858 „ C = 54.82; H = 8.02.  
 $\text{C}_8\text{H}_{14}\text{O}_4$  requires C = 55.18; H = 8.05 per cent.

*Isopropylglutaric acid* melts at 94—95°. It is readily soluble in water, and crystallises from the hot, concentrated solution, on cooling, in magnificent, colourless prisms; it is sparingly soluble in concentrated hydrochloric acid, and is, therefore, most economically purified by saturating the aqueous solution with hydrogen chloride.

The finely powdered crystals dissolve readily in alcohol or ether, and moderately in cold benzene, but the acid is almost insoluble in light petroleum.

#### *Salts of Isopropylglutaric acid.*

The *silver salt*,  $\text{C}_8\text{H}_{12}\text{Ag}_2\text{O}_4$  was prepared by adding silver nitrate to a slightly alkaline and fairly concentrated solution of the ammonium salt; the white flocculent precipitate was collected, washed with water, dried at 100°, and analysed.

- I. 0.2510 gave 0.2239  $\text{CO}_2$ , 0.0702  $\text{H}_2\text{O}$ , and 0.1396 Ag. C = 24.55  
 H = 3.10; Ag = 55.58.  
 II. 0.2487, on ignition, gave 0.1385 Ag. Ag = 55.70.  
 $\text{C}_8\text{H}_{12}\text{Ag}_2\text{O}_4$  requires C = 24.74; H = 3.10; Ag = 55.65 per cent.

A dilute neutral solution of ammonium isopropylglutarate gives a precipitate with *barium nitrate* or *calcium chloride*. *Copper sulphate*



gives a bright green, gelatinous precipitate, and *lead acetate*, on warming, a white, flocculent precipitate.

*Ethyllic Isopropylglutarate*,  $\text{COOC}_2\text{H}_5 \cdot \text{CH}(\text{C}_3\text{H}_7) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ .

This ethereal salt was prepared by dissolving the crude acid (obtained by heating pure isopropylpropanetricarboxylic acid at  $200^\circ$ ) in 4 vols. of absolute alcohol, and adding 1.5 vols. of concentrated sulphuric acid. After standing for two days, water was added, the oily ethereal salt extracted with ether, the ethereal solution washed with water and sodium carbonate, dried over anhydrous potassium carbonate, and the residual oil purified by distillation under reduced pressure.

Ethyllic isopropylglutarate is a colourless oil, having a strong, ethereal odour; it boils at  $158\text{--}160^\circ$  (45 mm.).

0.1251 gave 0.2860  $\text{CO}_2$  and 0.1079  $\text{H}_2\text{O}$ .  $\text{C} = 62.35$ ;  $\text{H} = 9.59$ .

$\text{C}_{12}\text{H}_{22}\text{O}_4$  requires  $\text{C} = 62.61$ ;  $\text{H} = 9.56$  per cent.

*Isopropylglutaric Anhydride*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}(\text{C}_3\text{H}_7) \cdot \text{CO} \end{array} > \text{O}$ .

This is readily prepared from isopropylpropanetricarboxylic acid by heating it at  $200^\circ$  until the evolution of carbon dioxide has ceased, dissolving the residue in freshly distilled acetic anhydride, heating the solution to boiling for 10 minutes, and then placing it over solid potash in a vacuum desiccator. After some days, the crystals of the anhydride are collected, left in contact with porous porcelain until colourless, and then recrystallised from boiling light petroleum (b. p.  $50\text{--}60^\circ$ ).

The following results were obtained on analysis.

0.1448 gave 0.3280  $\text{CO}_2$  and 0.1007  $\text{H}_2\text{O}$ .  $\text{C} = 61.77$ ;  $\text{H} = 7.72$ .

0.1490 „ 0.3336 „ „ 0.1017 „  $\text{C} = 61.06$ ;  $\text{H} = 7.58$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.54$ ;  $\text{H} = 7.68$  per cent.

*Isopropylglutaric anhydride* melts at about  $53^\circ$ , but not quite sharply, and the melted substance, on cooling, sets to a transparent, jelly-like mass, which, on rubbing, soon becomes crystalline and opaque. It is only sparingly soluble, even in boiling light petroleum (b. p.  $50\text{--}60^\circ$ ), and is almost completely deposited on cooling in very voluminous, feathery masses, consisting of slender needles, somewhat resembling cotton wool in appearance. It melts in boiling water, and dissolves only very slowly; on concentrating the solution and allowing it to stand, isopropylglutaric acid separates in magnificent, colourless prisms.

*Isopropylglutaranilic acid*,  $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{C}_3\text{H}_7)\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ ,  
or  $\text{COOH}\cdot\text{CH}(\text{C}_3\text{H}_7)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  (?).

In order to prepare this substance, 0.9 gram of pure isopropylglutaric anhydride was dissolved in 5 c.c. of pure dry benzene, and 0.7 gram of freshly distilled aniline added; this occasioned a considerable rise of temperature, and in about a minute the whole crystallised. The crystals were collected, drained on porous porcelain, and recrystallised from dilute methylic alcohol, when beautiful, colourless, glistening crystals were obtained, which gave the following results on analysis.

0.1384 gave 6.8 c.c. moist nitrogen at  $18^\circ$  and 755 mm.  $\text{N} = 5.64$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.62$  per cent.

*Isopropylglutaranilic acid* softens at  $150^\circ$ , and melts at  $158\text{--}159^\circ$ . It is readily soluble in alcohol, but only sparingly in benzene, light petroleum, or water. It does not appear to give off water, even when heated at  $250^\circ$ , but when heated to boiling for some time in a test-tube, decomposition takes place, probably with formation of the anil; as, however, the product was not readily purified, and I had very little substance at my disposal, the matter was not further investigated.

#### *Oxidation of Isopropylglutaric acid.*

Isopropylglutaric acid is only very slowly attacked by potassium dichromate and sulphuric acid even on boiling; 10 grams of the acid heated to boiling with 15 grams of potassium dichromate, 40 grams of concentrated sulphuric acid, and 300 c.c. of water for 10 days in a reflux apparatus, still contained unreduced chromic acid. The oxidation takes place, however, much more rapidly when the acid (10 grams) is digested with chromic acid (30 grams) and sulphuric acid (50 grams, diluted with 200 c.c. of water), the reduction of the chromic acid being complete after three days' boiling. The product from both experiments was distilled with steam until the condensed water ceased to have an acid reaction, the distillate was boiled with excess of barium carbonate, filtered, the filtrate evaporated to a small bulk, and precipitated with silver nitrate. The white crystalline silver salt was collected with the aid of the pump, washed with water, dissolved in boiling water, the hot solution filtered from traces of reduced silver, and allowed to stand; the glistening crystals of pure silver acetate which separated were collected, dried at  $100^\circ$ , and analysed.

0.1940, on ignition, gave 0.1252 Ag.  $\text{Ag} = 64.54$ .

$\text{CH}_3\cdot\text{COOAg}$  requires  $\text{Ag} = 64.67$  per cent.

The residue from the steam distillation was boiled with excess of

caustic soda, filtered from the chromium hydroxide, and the latter repeatedly washed with water; the combined liquors were then evaporated to a small bulk, acidified, and extracted three times with pure ether (A), and then again 30 times with pure ether (B).

The ethereal solution A, on evaporation, deposited a greenish crystalline acid, which, on recrystallisation from hydrochloric acid, at once yielded an acid, melting at 92—95°, which proved to be unattacked isopropylglutaric acid.

0.1489 gave 0.2991 CO<sub>2</sub> and 0.1075 H<sub>2</sub>O. C = 54.78; H = 8.02.

C<sub>8</sub>H<sub>14</sub>O<sub>2</sub> requires C = 55.18; H = 8.05 per cent.

The ethereal solution B, on evaporation, yielded a greenish crystalline mass, which contained only slight traces of isopropylglutaric acid. On repeatedly fractionally crystallising this substance from hydrochloric acid, beautiful colourless crystals were ultimately obtained, which melted at 183—185°, and consisted of pure succinic acid, as the following analysis shows:

0.1100 gave 0.1639 CO<sub>2</sub> and 0.0523 H<sub>2</sub>O. C = 40.66; H = 5.28.

C<sub>4</sub>H<sub>6</sub>O<sub>4</sub> requires C = 40.68; H = 5.10 per cent.

No other acids could be isolated from the products of the oxidation, and it therefore follows that when boiled with chromic acid and sulphuric acid, isopropylglutaric acid is oxidised with formation of acetic and succinic acids.

*Action of Ethylic α-Bromotrimethylpropionate on the Sodium Derivative of Ethylic Malonate in Alcoholic Solution.*

In studying this decomposition, sodium (6 grams) was dissolved in alcohol (75 grams) in a flask connected with a reflux condenser, ethylic malonate (40 grams) and ethylic α-bromotrimethylpropionate (56 grams) were added, and the whole allowed to stand for some time.

Very little action seemed to take place in the cold, but, on gently warming on a water bath, sodium bromide separated rapidly, the separation, after half an hour, being apparently so complete that in the earlier experiments the action was stopped at the end of this time; subsequently, however, it was found that a very much larger yield of condensation product could be obtained if the liquid was kept in vigorous ebullition for 2—3 days. At the end of this time, the alcohol was distilled off from a salt bath, the residue mixed with water, the oil which was precipitated extracted with ether, the ethereal solution washed, well dried over calcium chloride, the ether distilled off, and the light brown, oily residue fractionated under reduced pressure (100 mm.).

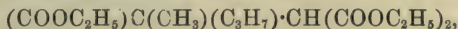


About half of this product distilled between  $125^{\circ}$  and  $145^{\circ}$ , the thermometer then rose rapidly, the greater bulk (22 grams) passing over between  $222^{\circ}$  and  $230^{\circ}$  (100 mm.); the latter, on refractionation, distilled for the most part constantly at  $220^{\circ}$  (100 mm.) as a colourless oil, which gave the following numbers on analysis:

0.1501 gave 0.3255  $\text{CO}_2$  and 0.1168  $\text{H}_2\text{O}$ . C = 59.14; H = 8.65.

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires C = 59.60; H = 8.61 per cent.

The careful examination of this substance showed that it was not ethylic methylisopropylethanetricarboxylate,



but that it consisted of very nearly pure ethylic isopropylpropanetricarboxylate (which it was expected would be formed during this reaction), identical with the product obtained by condensing ethylic isopropylacrylate with the sodium derivative of ethylic malonate (p. 1491); this was proved in the following way.

The ethereal salt was hydrolysed with alcoholic potash, and the tricarboxylic acid isolated and purified exactly as described in the case of isopropylpropanetricarboxylic acid (p. 1492). The crystalline product, like the acid just named, melted at  $163\text{--}165^{\circ}$  with decomposition, and gave, on analysis, the following numbers:

0.1695 gave 0.3064  $\text{CO}_2$  and 0.1002  $\text{H}_2\text{O}$ . C = 49.30; H = 6.56.

$\text{C}_9\text{H}_{14}\text{O}_6$  requires C = 49.54; H = 6.42 per cent.

On heating this acid at  $200^{\circ}$ , carbon dioxide was evolved, and the residue, after being twice recrystallised from hydrochloric acid, melted at  $94\text{--}95^{\circ}$ , and consisted of isopropylglutaric acid, as was shown by converting it into its anhydride (m. p.  $53^{\circ}$ ), and into isopropylglutaranilic acid (m. p.  $157\text{--}159^{\circ}$ ), and also from the results obtained on analysis.

0.1472 gave 0.2956  $\text{CO}_2$  and 0.1065  $\text{H}_2\text{O}$ . C = 54.77; H = 8.10.

$\text{C}_8\text{H}_{14}\text{O}_4$  requires C = 55.18; H = 8.05 per cent.

There can be no doubt that the product of the action of ethylic bromotrimethylpropionate on the sodium derivative of ethylic malonate in alcoholic solution, is ethylic isopropylpropanetricarboxylate.

*Action of Ethylic Bromotrimethylpropionate on the Sodium Derivative of Ethylic Malonate in Xylene Solution.*

As stated in the introduction to this paper, it has often been found that in cases where a glutaric acid derivative is formed by the action of an  $\alpha$ -bromo-ethereal salt on the sodium derivative of ethylic malonate in alcoholic solution, a widely different result may be



obtained by substituting xylene for alcohol as the solvent, the product consisting then for the most part of a derivative of succinic acid. In order to determine whether this would be the case in the present instance, the following experiment was made. Sodium (3 grams) was melted under boiling xylene and the whole violently agitated so as to bring the sodium into a state of the finest possible division, ethylic malonate (20 grams) was then added, and the whole heated to boiling in a reflux apparatus until the sodium had completely disappeared; ethylic  $\alpha$ -bromotrimethylpropionate (28 grams) was then added, and the mixture heated to boiling for two days. The brownish product was shaken with water and a quantity of ether, the ethereal solution was separated, washed well with water and dilute hydrochloric acid, dried over calcium chloride, and the ether and xylene distilled off, at first under ordinary, but subsequently under reduced pressure. On fractionating the oily residue under 100 mm. pressure, the greater portion distilled below  $160^{\circ}$ , only about 6 grams passing over between  $210^{\circ}$  and  $230^{\circ}$ . The latter portion, on refractionation, passed over between  $218^{\circ}$  and  $222^{\circ}$  as a colourless oil, which, on analysis, gave the following results.

0.1680 gave 0.3632  $\text{CO}_2$  and 0.1296  $\text{H}_2\text{O}$ .  $\text{C} = 58.96$ ;  $\text{H} = 8.58$ .

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires  $\text{C} = 59.60$ ;  $\text{H} = 8.61$  per cent.

That this substance consisted, in this case also, at all events for the most part, of ethylic isopropylpropanetricarboxylate was proved in the following way.

The ethereal salt, on hydrolysis, yielded a tricarboxylic acid which melted at  $163^{\circ}$ , and at slightly higher temperatures decomposed, yielding an acid which, after recrystallisation, melted at  $94$ – $95^{\circ}$ ; this acid gave an anhydride melting at  $53^{\circ}$ , and an anilic acid melting at  $156$ – $158^{\circ}$ ; it was, therefore, evidently isopropylglutaric acid.

It is, of course, quite possible that, in this experiment, some ethylic methylisopropylethanetricarboxylate may have been formed, but the quantity present in the product of the reaction can only have been small.

*Action of Phenoxyethylic Bromide,  $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , on the Sodium Derivative of Ethylic Dimethylpropanetricarboxylate,*  
 $(\text{COOC}_2\text{H}_5)_2\text{CH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ .

The reason for investigating this reaction has been mentioned in the introduction to this paper; the experiment was carried out as follows.

Sodium (5 grams) was dissolved in absolute alcohol (70 grams) in a flask connected with a reflux apparatus; the solution, when nearly cold, was mixed with ethylic dimethylpropanetricarboxylate (62

grams), then phenoxyethylic bromide (45 grams) was added, and the whole gradually heated to boiling on a water bath. No action appeared to take place until the temperature had risen to about  $50^{\circ}$ , then sodium bromide began to separate rapidly, and after heating to boiling for four hours the liquid had a neutral reaction. Water was now added, the oily product extracted four times with ether, the ethereal solution well washed with water, dried over calcium chloride, and evaporated, when 88 grams of a very slightly coloured oil was obtained; this was not analysed but directly converted into the corresponding acid by hydrolysis.

For this purpose, the oil was heated for four hours in a reflux apparatus with potash (80 grams), dissolved in pure methylic alcohol, the bulk of the alcohol was then distilled off, water added, and the neutral oil (phenoxyethyl ethyl ether,  $C_6H_5O \cdot CH_2 \cdot CH_2 \cdot OC_2H_5$ , see p. 1503) which separated was extracted with ether; the aqueous solution was then evaporated on a water bath until quite free from alcohol, and the cold, moderately concentrated solution acidified with hydrochloric acid. This caused the precipitation of a viscous oil, which, however, on adding ice and shaking well, solidified in the course of half an hour, to a hard, ochre-coloured mass. In order to purify it, the crude substance was ground up with water, well washed by means of the pump, dissolved in dilute sodium carbonate, and the brown solution heated on a water bath with purified animal charcoal for an hour; after filtration, the liquid was very much lighter coloured, and, on the addition of hydrochloric acid, gave an almost colourless, oily precipitate, which, however, very rapidly solidified. The solid acid was collected, washed with water, left in contact with porous porcelain for a few days, and then purified by recrystallisation from dilute acetic acid; it was thus obtained in the form of colourless prisms, which, on analysis, gave the following numbers.

- I. 0.1106 gave 0.2676  $CO_2$  and 0.0626  $H_2O$ . C = 65.99; H = 6.33.  
 II. 0.1392 „ 0.3381 „ „ 0.0750 „ C = 66.23; H = 5.98.  
 ( $C_6H_5O \cdot CH_2 \cdot CH_2$ )<sub>2</sub>C(COOH)<sub>2</sub> requires C = 66.28; H = 5.81 p.c.

This acid melted at about  $150$ — $152^{\circ}$  with decomposition, and was found, on examination, to be diphenoxyethylmalonic acid, identical with the acid which was subsequently prepared by the action of phenoxyethylic bromide on the sodium derivative of ethylic malonate, and is described in a previous paper (Bentley, Haworth, and Perkin, this vol., 169).

#### *Salts of Diphenoxyethylmalonic acid.*

These have not been previously described.

The *silver salt*,  $(C_6H_5O \cdot CH_2 \cdot CH_2)C(COOAg)_2$ , was obtained as a curdy, white precipitate on adding an excess of silver nitrate to

the slightly alkaline solution of the ammonium salt of the acid. It was collected, well washed with water, dried on a porous plate over sulphuric acid and then for a short time in the water oven.

0.1981 gave 0.2907  $\text{CO}_2$ , 0.0621  $\text{H}_2\text{O}$ , and 0.0759 Ag.  $\text{C} = 40.09$ ;  $\text{H} = 3.48$ ;  $\text{Ag} = 38.31$ .

$\text{C}_{19}\text{H}_{10}\text{Ag}_2\text{O}_6$  requires  $\text{C} = 40.86$ ;  $\text{H} = 3.22$ ;  $\text{Ag} = 38.71$  per cent.

The dilute solution of the ammonium salt of this acid shows the following behaviour with reagents.

*Calcium Chloride*.—A heavy, white, amorphous precipitate.

*Barium Chloride*.—A white, amorphous precipitate, which, on boiling, apparently becomes crystalline.

*Copper Sulphate*.—A light blue gelatinous precipitate, insoluble in water.

*Lead Acetate*.—A white, gelatinous precipitate, which, on boiling, cakes together to a caseous mass quite insoluble in water.

*Diphenoxyethylacetic acid*,  $(\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH}$ .

When diphenoxyethylmalonic acid is heated at  $180^\circ$ , it is rapidly decomposed with evolution of carbon dioxide and formation of diphenoxyethylacetic acid, the reaction taking place quantitatively, as is shown by the following experiment.

9.0224 grams of the pure dibasic acid, heated in a small flask in an oil bath, lost 1.1574 gram of  $\text{CO}_2 = 12.83$  per cent., whereas according to the equation

$(\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{C}(\text{COOH})_2 = (\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH} + \text{CO}_2$ , the calculated loss is 12.78 per cent.

The residual monobasic acid was dissolved in dilute sodium carbonate, and the solution digested with purified animal charcoal and filtered; the filtrate was then acidified with hydrochloric acid, and the precipitated acid, which at first was oily but which soon solidified to a hard cake, was washed with water, and purified by recrystallisation from dilute alcohol.

0.1264 gave 0.3334  $\text{CO}_2$  and 0.0751  $\text{H}_2\text{O}$ .  $\text{C} = 71.93$ ;  $\text{H} = 6.60$ .  $(\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH}$  requires  $\text{C} = 72.00$ ;  $\text{H} = 6.67$  p. c.

It melts at  $87-88^\circ$  and is identical with the acid obtained from the sodium compound of ethylic malonate by the action of phenoxyethyl bromide (Bentley, Haworth, and Perkin, this vol., 169). The following salts of this acid, which have not been described, were prepared when the acid was first obtained.

The *silver salt*,  $(\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOAg}$ , obtained on adding silver nitrate to a slightly alkaline solution of the ammonium salt of the acid, is a caseous precipitate, which after repeated washing



with water, becomes quite brittle. It was ground up, washed well with water and then with methylic alcohol, and dried over sulphuric acid. On analysis the following results were obtained.

I. 0.2480 gave 0.4830  $\text{CO}_2$ , 0.1068  $\text{H}_2\text{O}$ , and 0.0646 Ag.  $\text{C} = 53.11$ ;  $\text{H} = 4.78$ ;  $\text{Ag} = 26.05$ .

II. 0.1240 gave 0.0328 Ag.  $\text{Ag} = 26.45$ .

$\text{C}_{18}\text{H}_{19}\text{AgO}_4$  requires  $\text{C} = 53.07$ ;  $\text{H} = 4.67$ ;  $\text{Ag} = 26.53$  per cent.

The dilute neutral solution of the ammonium salt shows the following behaviour with reagents.

*Calcium Chloride*.—A white gelatinous precipitate, almost insoluble in water.

*Barium Nitrate*.—No precipitate even on boiling.

*Copper Sulphate*.—A light blue, caseous precipitate, which, on boiling, becomes granular.

*Lead acetate*.—A white, caseous precipitate, which, on warming with water, becomes pasty and apparently decomposes.

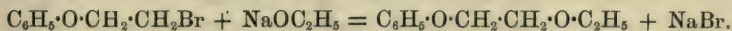
*Phenoxyethyl Ethyl Ether*,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$ .

During the hydrolysis of the product of the action of phenoxy-ethylic bromide on the sodium compound of ethylic dimethylpropanetricarboxylate it was found, as stated on p. 1501, that a considerable quantity of a neutral substance was formed. The product from several experiments was collected, dissolved in ether, washed with water, dried over calcium chloride, and the ethereal solution evaporated; on submitting the oily residue to fractional distillation, the greater portion boiled at  $227\text{--}229^\circ$ , and gave the following results on analysis.

0.1502 gave 0.3974  $\text{CO}_2$  and 0.1150  $\text{H}_2\text{O}$ .  $\text{C} = 72.16$ ;  $\text{H} = 8.50$ .

$\text{C}_{10}\text{H}_{14}\text{O}_2$  requires  $\text{C} = 72.28$ ;  $\text{H} = 8.43$  per cent.

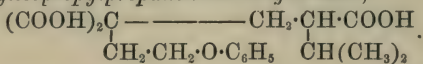
There can be no doubt that this substance is phenoxyethyl ethyl ether, produced by the action of sodium ethoxide on the phenoxy-ethylic bromide used in the experiments.



It is a colourless oil possessing a penetrating odour somewhat similar to that of benzyl ethyl ether,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$ .



*Action of Phenoxyethyllic Bromide,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Br$ , on the Sodium Derivative of Ethylic Isopropylpropanetricarboxylate. Formation of Phenoxyethylisopropylpropanetricarboxylic acid,*



In carrying out this experiment, 1.2 gram of sodium was dissolved in 15 grams of absolute alcohol, and, after cooling well, 15 grams of ethylic isopropylpropanetricarboxylate was added; the yellow solution thus produced was mixed with 11 grams of phenoxyethyllic bromide, and the whole heated in a reflux apparatus on the water bath; at first very little action appeared to take place, but after a time the liquid became suddenly cloudy and quantities of sodium bromide separated rapidly.

After heating for 10 hours to boiling, the product, which was still alkaline, was mixed with water, and extracted five times with ether; the ethereal solution was washed well, dried over calcium chloride, and evaporated, when 22 grams of a yellow oil were obtained, which did not solidify after standing over sulphuric acid in a vacuum for two days.

This oil, on examination, proved to be a mixture; it was therefore not analysed but converted into the corresponding acids, by boiling for two hours with methyl alcoholic potash (20 grams). The alkaline product was evaporated until free from alcohol, extracted with ether to remove any neutral oil (phenoxyethyl ethyl ether), again evaporated, the residue dissolved in water, and, after cooling well, acidified with dilute hydrochloric acid. The yellowish semi-solid mass which was thus precipitated soon became quite solid, especially after adding ice and shaking well; it was collected, ground up with water, and washed with the aid of the pump, the mother liquors being preserved for subsequent investigation (see below). In order to purify the crude acid thus obtained, it was dissolved in dilute sodium carbonate, digested with purified animal charcoal, filtered, and the filtrate, after cooling with ice, acidified with hydrochloric acid, the whole being stirred during the operation. In this way an almost colourless precipitate of nearly pure phenoxyethylisopropylpropanetricarboxylic acid was obtained, which, after washing and drying, resembled starch powder in appearance; in this condition, it melted at  $178-180^\circ$  with vigorous evolution of gas.

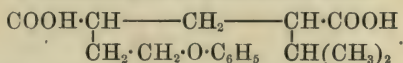
This product was now dissolved in much pure ether, the ethereal solution evaporated to a small bulk, and allowed to stand in a closed flask, when the pure acid separated in hard, glistening, crystalline crusts; these crystals were washed with ether, dried at  $100^\circ$ , and analysed with the following results,

- I. 0.1080 gave 0.2368  $\text{CO}_2$  and 0.0640  $\text{H}_2\text{O}$ .  $\text{C} = 59.80$ ;  $\text{H} = 6.58$ .  
 II. 0.1032 „ 0.2286 „ „ 0.0630 „  $\text{C} = 60.41$ ;  $\text{H} = 6.78$ .  
 $\text{C}_{17}\text{H}_{22}\text{O}_7$  requires  $\text{C} = 60.36$ ;  $\text{H} = 6.51$  per cent.

*Phenoxyethylisopropylpropanetricarboxylic acid*, when heated in a capillary tube, softens at  $178^\circ$  and melts at  $179$ – $180^\circ$  with rapid decomposition into carbon dioxide and the corresponding dibasic acid. It is readily soluble in alcohol, but only sparingly in benzene, light petroleum, chloroform, and cold water; the finely divided substance dissolves with difficulty in boiling water, and crystallises out again on cooling almost completely in curious nodular masses.

The yield of the phenoxy-acid obtained by the above method is only 4–5 grams from 15 grams of ethylic isopropylpropanetricarboxylate, whereas, assuming this ethereal salt to be pure, over 17 grams should have been obtained. One reason for this is the formation of considerable quantities of phenoxyethyl ethyl ether during the reaction, and thus a portion of the ethylic isopropylpropanetricarboxylate employed takes no part in the decomposition, and remains unchanged in the crude product of the reaction. On hydrolysing this crude product, as described above, and precipitating the phenoxy-acid with hydrochloric acid, isopropylpropanetricarboxylic acid remains in the filtrate and in the mother liquors from the purification of this acid, and is easily recovered by neutralising with sodium carbonate, evaporating to a small bulk, acidifying, and extracting 10 times with pure ether. After drying over calcium chloride and distilling off the ether, the oily residue was etherified by treatment with alcohol and sulphuric acid, and the ethereal salt, after purification by distillation under reduced pressure, was employed in subsequent operations. Ultimately a good yield of phenoxyethylisopropylpropanetricarboxylic acid may be obtained in this way; but the preparation of this acid is, nevertheless, a very tedious one, many weeks being required in preparing it—even in small quantities.

*Phenoxyethylisopropylglutaric acid,*



When phenoxyethylisopropylpropanetricarboxylic acid is heated at  $180$ – $190^\circ$ , it rapidly loses carbon dioxide, and, apparently also, water vapour, and is converted into a colourless oil which, on cooling, does not solidify, even on long standing, and may possibly consist of the anhydride of the dibasic acid. It was dissolved in boiling dilute sodium carbonate, the solution filtered, acidified, and extracted with pure ether, the ethereal solution dried over calcium chloride, evaporated at a low temperature, and the residual oil allowed to stand for two

days, when it had almost completely solidified. Considerable difficulty was experienced in endeavouring to recrystallise the acid, but ultimately this was accomplished by dissolving the crude substance in a large quantity of light petroleum (b. p. 100—120°), boiling with animal charcoal, filtering, and allowing the solution to stand for some days exposed to the air; nodular crystals then separated, which, after washing with light petroleum (b. p. 40—45°), gave the following numbers on analysis.

0·1317 gave 0·3161 CO<sub>2</sub> and 0·0899 H<sub>2</sub>O. C = 65·43; H = 7·50.

0·1431 „ 0·3415 „ „ 0·0969 „ C = 65·10; H = 7·51.

C<sub>16</sub>H<sub>22</sub>O<sub>5</sub> requires C = 65·30; H = 7·49 per cent.

*Phenoxyethylisopropylglutaric acid* melts at about 90—93°; it is readily soluble in alcohol and ether, but almost insoluble in water. When heated for some time in a water bath, it is converted into an oil which, on cooling, sets to a transparent jelly; this does not crystallise, even on rubbing with a crystal of the pure acid, and, therefore, may possibly be the anhydride of the acid, especially as it dissolves in cold sodium carbonate with difficulty.

ACTION OF ETHYLIC  $\beta$ -IODOPROPIONATE ON  
THE SODIUM DERIVATIVE OF ETHYLIC  
ISOPROPYLMALONATE.

BY

J. L. HEINKE

AND

W. H. PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1896.]





97. Action of ethylic  $\beta$ -iodopropionate on the sodium derivative of ethylic isopropylmalonate.

By J. L. HEINKE and W. H. PERKIN, jun.

THESE experiments which were instituted, as explained in the introduction to the preceding paper, with the object of obtaining additional evidence of the constitution of isopropylglutaric acid, were conducted as follows.

Sodium (6 grams) was dissolved in absolute alcohol (75 grams), the solution cooled, and *very carefully purified* ethylic isopropylmalonate (55 grams) and ethylic  $\beta$ -iodopropionate (50 grams) were added, when a somewhat energetic action set in, the mixture becoming quite hot. As soon as the action had subsided, the mixture was heated for four hours on a water bath, in a reflux apparatus, water was then added, the oily product extracted three times with ether, the ethereal solution washed well with water containing a little sulphurous acid, to remove traces of iodine, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure (100 mm.).

Between 150° and 210°, about 20 grams came over, the thermometer then rose rapidly to 220°, most of the residue distilling at 225—235°, and this portion, on refractionation, distilled almost con-

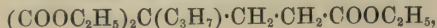
stantly at 228—230° (100 mm.) as a thick, colourless oil, which, on analysis, gave the following numbers.

0.1604 gave 0.3490 CO<sub>2</sub> and 0.1236 H<sub>2</sub>O. C = 59.34; H = 8.56.

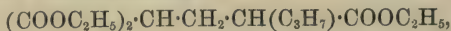
0.1444 „ 0.3159 „ „ 0.1123 „ C = 59.64; H = 8.65.

C<sub>15</sub>H<sub>26</sub>O<sub>6</sub> requires C = 59.60; H = 8.61 per cent.

This ethylic  $\alpha$ -isopropylpropane- $\alpha\alpha\alpha_1$ -tricarboxylate,



is isomeric with the ethereal salt,



described in the preceding paper, and obtained by the action of ethylic  $\alpha$ -bromotrimethylpropionate on the sodium derivative of ethylic malonate, or by condensing ethylic malonate with ethylic isopropylacrylate. Both of these ethereal salts are thick, colourless oils, the former boiling apparently rather higher than the latter.

*Hydrolysis of Ethylic  $\alpha$ -Isopropylpropane- $\alpha\alpha\alpha_1$ -tricarboxylate. Formation of  $\alpha$ -Isopropylpropane- $\alpha\alpha\alpha_1$ -tricarboxylic acid, and of Isopropylglutaric acid.*

The hydrolysis of ethylic isopropylpropanetricarboxylate was carried out by boiling the pure substance in a reflux apparatus with twice the calculated quantity of alcoholic potash for four hours; the product was mixed with water, evaporated on a water bath till free from alcohol, acidified, and extracted 10 times with pure ether. The ethereal solution was dried over calcium chloride and evaporated at a low temperature, when an oily acid was obtained which did not crystallise, even when left for some days over sulphuric acid in a vacuum. The analysis gave numbers indicating that the substance consisted of nearly pure  $\alpha$ -isopropylpropane- $\alpha\alpha\alpha_1$ -tricarboxylic acid.

0.1423 gave 0.2607 CO<sub>2</sub> and 0.0810 H<sub>2</sub>O. C = 49.95; H = 6.33.

C<sub>9</sub>H<sub>14</sub>O<sub>6</sub> requires C = 49.54; H = 6.41 per cent.

This acid differs from its isomeride, described in the preceding paper, in that, when its solution in water is saturated with hydrogen chloride, the acid does not separate in a crystalline form, and it has, so far, not been possible to obtain the substance in a crystalline state by treatment with various solvents.

When heated at 200°, the tribasic acid is decomposed with evolution of carbon dioxide and formation of isopropylglutaric acid; this was best purified as follows:—The crude acid was digested with acetic anhydride, and then converted into its anhydride; this was fractionated under reduced pressure, when almost the whole distilled at 217—222° (100 mm.) as a colourless oil which rapidly solidified on

standing. The crystals were spread on porous porcelain until free from oily mother liquor, and the residual, colourless, crystalline mass recrystallised from light petroleum.

0.1762 gave 0.3969  $\text{CO}_2$  and 0.1210  $\text{H}_2\text{O}$ .  $\text{C} = 61.43$ ;  $\text{H} = 7.63$

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.54$ ;  $\text{H} = 7.68$  per cent.

This anhydride melts at  $53\text{--}54^\circ$ , and crystallises from light petroleum in the same characteristic woolly masses as the isopropylglutaric anhydride described in the previous paper. When treated with aniline in benzene solution, it yields isopropylglutaranilic acid (m. p.  $158^\circ$ ), which was analysed with the following result.

0.2266 gave 11 c.c. moist nitrogen at  $15^\circ$  and 755 mm.  $\text{N} = 5.65$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.62$  per cent.

Lastly, if the anhydride be dissolved in boiling water, the solution concentrated, saturated with hydrogen chloride, and allowed to stand, hard, colourless crystals of isopropylglutaric acid separate, which melt at  $94\text{--}95^\circ$ , and resemble in all respects the crystals of isopropylglutaric acid obtained in the manner described in the previous paper.

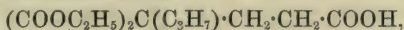
0.1470 gave 0.2963  $\text{CO}_2$  and 0.1067  $\text{H}_2\text{O}$ .  $\text{C} = 55.07$ ;  $\text{H} = 7.93$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

While these experiments were in progress and nearly completed, we heard from Professor Auwers that he had instituted similar experiments in conjunction with Mr. A. W. Titherley.\*

These chemists studied the action of ethylic  $\beta$ -iodopropionate on the sodium derivative of ethylic isopropylmalonate, and thus obtained an ethereal salt boiling at  $197^\circ$  (33 mm.), which, although not analysed, was obviously identical with the ethylic  $\alpha$ -isopropylpropane-*aaa*<sub>1</sub>-tricarboxylate obtained by us, and which distilled, as stated above, at  $228\text{--}230^\circ$  (100 mm.).

This ethereal salt was then hydrolysed by boiling with hydrochloric acid, and thus converted into a remarkably stable crystalline diethylic salt of the formula



(m. p.  $68\text{--}69^\circ$ ), which appears to resist the further action of the acid; when boiled with alcoholic soda, however, it is hydrolysed, with formation of a syrupy acid, which evidently consists of not quite pure isopropylglutaric acid. As soon as Professor Auwers heard that we were investigating this subject and had already obtained pure isopropylglutaric acid, he did not continue his experiments, but kindly left the completion of the research to us.

\* The results of these experiments have since been published in the *Annalen*, 1896, **292**, 217.



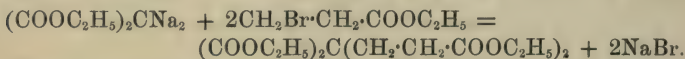
*Pentane- $\alpha\gamma\gamma\alpha_1$ -tetracarboxylic acid*,  $(\text{COOH})_2\text{C}(\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH})_2$ .

In our first experiments on the action of ethylic  $\beta$ -iodopropionate on the sodium derivative of ethylic isopropylmalonate, a sample of the latter was employed which boiled at  $209\text{--}211^\circ$ , and which, although it had been carefully prepared, must evidently, from the results subsequently obtained, have contained some unchanged ethylic malonate. This fraction was treated with sodium and ethylic  $\beta$ -iodopropionate, as described on p. 1506, and the product distilled under reduced pressure (30 mm.), when, after the ethylic isopropylpropanetricarboxylate had passed over, a considerable fraction was obtained, boiling at  $230\text{--}235^\circ$ . After again fractionating, this gave the following results on analysis.

0.1411 gave 0.2957  $\text{CO}_2$  and 0.1019  $\text{H}_2\text{O}$ . C = 57.13; H = 8.03.

$\text{C}_{17}\text{H}_{28}\text{O}_8$  requires C = 56.67; H = 7.78 per cent.

The further examination of this substance showed that it was ethylic pentane- $\alpha\gamma\gamma\alpha_1$ -tetracarboxylate, identical with the compound obtained by Emery (*Ber.*, 1891, **24**, 282) by treating the sodium compound of ethylic malonate with ethylic  $\beta$ -bromopropionate.



Emery gives the boiling point of his ethereal salt as  $215^\circ$  (13 mm.). From the ethereal salt, the corresponding tetracarboxylic acid, which is not described by Emery, may be obtained in the following way. It is hydrolysed by boiling with an excess of alcoholic potash for two hours in a reflux apparatus, the solution mixed with water, boiled until free from alcohol, evaporated to a small bulk, acidified, and extracted at least 30 times with pure ether, as the acid is only sparingly soluble in ether and very difficult to extract. After drying the ethereal solution over calcium chloride and evaporating to a small bulk, crystalline crusts are deposited on standing; these were collected, washed with ether, dissolved in a very little water, and the solution saturated with hydrogen chloride, when almost the whole of the acid separated as a colourless, sandy powder, which gave the following results on analysis.

0.1321 gave 0.2112  $\text{CO}_2$  and 0.0594  $\text{H}_2\text{O}$ . C = 43.61; H = 4.99.

$\text{C}_9\text{H}_{12}\text{O}_8$  requires C = 43.55; H = 4.84 per cent.

*Pentane- $\alpha\gamma\gamma\alpha_1$ -tetracarboxylic acid*, when heated in a capillary tube, decomposes rapidly at about  $185\text{--}187^\circ$  with vigorous evolution of gas, and formation of pentane- $\alpha\gamma\alpha_1$ -tricarboxylic acid.

*Pentane- $\alpha\gamma\alpha_1$ -tricarboxylic acid*,  $\text{COOH}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH})_2$ .

This acid was prepared by heating the corresponding tetracarboxylic acid at  $200^\circ$  until the evolution of carbon dioxide had ceased. The syrupy residue was dissolved in hot water, and the solution, after cooling, saturated with hydrogen chloride, but no crystallisation took place even on long standing; when, however, the solution was placed over solid potash in a vacuum desiccator, beautiful colourless prisms separated after some days; these were collected, dried at  $90^\circ$ , and analysed.

I. 0.1785 gave 0.3078  $\text{CO}_2$  and 0.1001  $\text{H}_2\text{O}$ . C = 47.03; H = 6.29.

II. 0.1431 „ 0.2478 „ „ 0.0768 „ C = 47.23; H = 5.97.

$\text{C}_8\text{H}_{12}\text{O}_6$  requires C = 47.06; H = 5.88 per cent.

*Pentane- $\alpha\gamma\alpha_1$ -tricarboxylic acid* melts at  $114\text{--}115^\circ$  with slight previous softening. Emery (*Ber.*, 1891, **24**, 284) gives the melting point at  $106\text{--}107^\circ$ .



ON  $\gamma$ -PHENOXY-DERIVATIVES OF MALONIC  
ACID AND ACETIC ACID, AND VARIOUS  
COMPOUNDS USED IN THE SYNTHESIS OF  
THESE ACIDS.

BY

WILLIAM HENRY BENTLEY,

EDWARD HAWORTH,

AND

WILLIAM HENRY PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1896.]



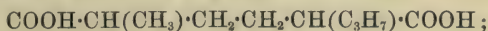


On  $\gamma$ -phenoxy-derivatives of malonic acid and acetic acid, and various compounds used in the synthesis of these acids.

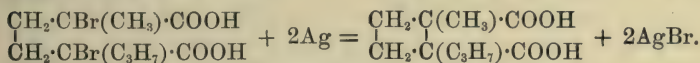
By WILLIAM HENRY BENTLEY, EDWARD HAWORTH, and WILLIAM HENRY PERKIN, jun.

THIS paper contains a description of a number of compounds which were prepared in the course of a research, not yet completed, on the synthesis of methylisopropyltetramethylenedicarboxylic acid,  $\text{CH}_2\cdot\text{C}(\text{CH}_3)\cdot\text{COOH}$   
 $\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_7)\cdot\text{COOH}$ . This acid possesses especial interest from the fact that its formula was for a long time considered as the most probable expression of the constitution of camphoric acid.

Our idea in attempting to synthesise this acid was to prepare in the first instance  $\alpha\alpha_1$ -methylisopropyladipic acid,

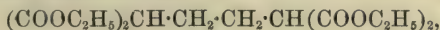


to brominate this acid and then to treat the dibromo-acid thus formed with finely divided silver.

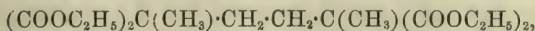


In attempting to synthesise  $\alpha\alpha_1$ -methylisopropyladipic acid we have met with unexpected difficulties.

It was known from the work of Bevan Lean (*Trans.*, 1894, **65**, 997; compare also Perkin and Prentice, *Trans.*, 1891, **59**, 819, and Guthzeit and Dressel, *Annalen*, 1890, **256**, 180—188), that, starting with ethylic butanetetracarboxylate,



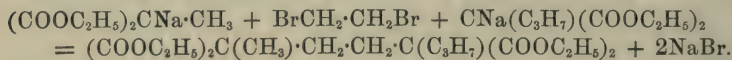
and treating this ethereal salt with sodium ethoxide and methylic iodide, and then again with sodium ethoxide and isopropyl iodide, it was not possible to obtain ethylic methylisopropylbutane tetracarboxylate from which the desired acid could easily have been prepared, because when this ethereal salt (1 mol.) is treated with sodium (1 atom) and methylic iodide (1 mol.) the dimethyl derivative,



is at once produced with regeneration of half of the ethylic butanetetracarboxylate, so that it was found necessary, in order to prepare methylisopropyladipic acid, to resort to indirect methods. The following experiments were therefore instituted, and although many of them gave interesting results, we have not been able, so far, in any

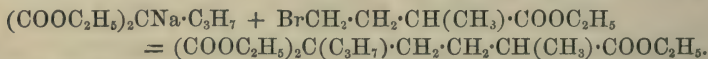
case to obtain sufficient of the methylisopropyladipic acid for analysis and an examination of its properties.

(1) The action of sodium ethoxide and ethylene dibromide (or chlorobromide) on various mixtures of ethylic methylmalonate and ethylic isopropylmalonate was studied in the hope that, in this way, ethylic methylisopropylbutanetetracarboxylate might be formed.



but, at the most, only very small quantities of this ethereal salt could be obtained, and from it no well defined acid could be isolated.

(2) Methylbutyrolactone,  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}_3 \\ | \quad \quad | \\ \text{O} \quad \quad \text{CO} \end{array}$ , was prepared and converted into *ethylic*  $\gamma$ -bromethylmethylacetate by treatment with hydrogen bromide and subsequent etherification; this ethereal salt was then digested with the sodium derivative of ethylic isopropylmalonate, when it was anticipated that the following decomposition would take place.



From this ethylic methylisopropylbutanetricarboxylate, the desired acid could then be obtained by hydrolysis and elimination of 1 mol. of carbon dioxide.

Unfortunately, during this reaction, the brom-ethereal salt is evidently for the most part decomposed into methylbutyrolactone and ethylic bromide, so that in this instance again very small quantities only of an ethereal salt of high boiling point were obtained.

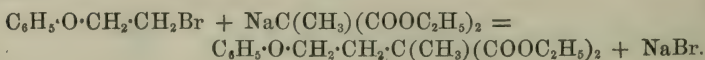
Some considerable difficulty was experienced in preparing methylbutyrolactone, and a number of experiments on the action of glycol chlorhydrin on the sodium compounds of ethylic methylmalonate, and ethylic methylacetoacetate, under widely different conditions, failed to give condensation products from which this lactone might readily have been prepared by hydrolysis.

Ultimately considerable quantities of methylbutyrolactone were obtained in the following way:—

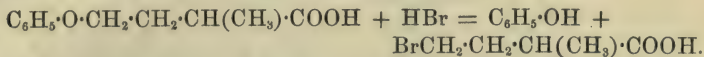
$\beta$ -Bromethyl phenyl ether was first prepared by the action of ethylene dibromide on sodium phenoxide in alcoholic solution,



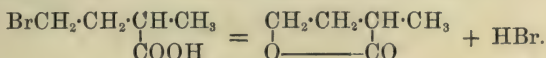
and from this, by digesting it with the sodium compound of ethylic methylmalonate, *ethylic*  $\gamma$ -phenoxyethyl- $\alpha$ -methylmalonate was obtained.



This ethereal salt on hydrolysis yields the corresponding acid, which, when heated at 180°, loses 1 mol. of carbon dioxide with formation of *γ*-phenoxyethylmethylacetic acid,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot COOH$ ; the latter, by the action of fuming hydrobromic acid, is decomposed into phenol and *γ*-bromomethylmethylacetic acid.

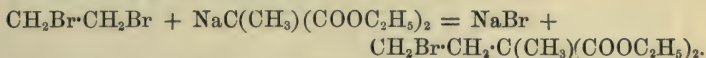


Boiling with sodium carbonate solution readily decomposes this bromo-acid with formation of methyl butyrolactone,

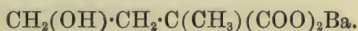


After these experiments had been completed, a paper by R. Marburg appeared in the *Berichte* (1895, **28**, 8) describing a different method for preparing methylbutyrolactone, which is briefly as follows:—

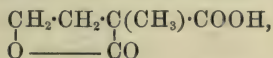
Ethylene dibromide is digested with the sodium derivative of ethylic methylmalonate, when the product of the action is found to contain ethylic *γ*-bromomethylmethylmalonate,



This ethylic salt, on hydrolysis with baryta water, yields the barium salt of *γ*-hydroxyethylmethylmalonic acid,



The free hydroxy acid is not capable of existence, as, on acidifying its barium salt, it at once decomposes with elimination of water and formation of *α*-methylbutyrolactonecarboxylic acid,



and this on dry distillation yields methylbutyrolactone with evolution of carbon dioxide. The properties of the substance prepared in this way are identical with those of the methylbutyrolactone obtained by us by the method described above.

During the course of this investigation many difficulties were encountered which necessitated the preparation and examination of a number of substances which at first sight may appear to have little connection with the synthesis mentioned above. Such of these substances as are mentioned in this communication may be tabulated for the sake of reference, they are the following:—

*Glycol phenyl ether*,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ .

*β*-chloroethyl phenyl ether,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Cl$ .



*β*-bromethyl phenyl ether,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Br$ .

*Ethylene diphenyl ether*,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_6H_5$ .

*Methylene diphenyl ether*,  $C_6H_5 \cdot O \cdot CH_2 \cdot O \cdot C_6H_5$ .

*γ*-Phenoxyethylmalonic acid,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(COOH)_2$ .

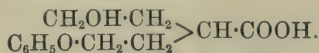
*γ*-Phenoxybutyric acid,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ .

*Butyrolactone*,  $\begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \\ | \quad \quad | \\ O \text{ ——— } CO \end{array}$ .

*Diphenoxyethylmalonic acid*,  $(C_6H_5O \cdot CH_2 \cdot CH_2)_2C(COOH)_2$ .

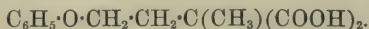
*Diphenoxyethylacetic acid*,  $(C_6H_5O \cdot CH_2 \cdot CH_2)_2CH \cdot COOH$ .

*β*-Phenoxyethyl-*γ*-hydroxybutyric acid,

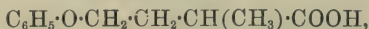


*β*-Ethoxyethyl phenyl ether,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_2H_5$ .

*γ*-Phenoxyethyl-*α*-methylmalonic acid,



*γ*-Phenoxyethyl-*α*-methylacetic acid,



*Methylbutyrolactone*,  $\begin{array}{c} CH_2 \cdot CH_2 \cdot CH \cdot CH_3 \\ | \quad \quad | \\ O \text{ ——— } CO \end{array}$ .

*α*-Methyl-*γ*-bromobutyric acid,  $CH_2Br \cdot CH_2 \cdot CH(CH_3) \cdot COOH$ .

A few of the above compounds have been prepared previously, and in these cases we have only given details where we have been able to effect improvements in the preparation.

We are still engaged in experiments on the preparation of methylisopropyltetramethylenedicarboxylic acid, and hope soon to be able to lay before the Society an account of the results obtained.

At the same time we are continuing the examination of some of the substances tabulated above, and especially interesting results are anticipated from the study of the hydrolysis of diphenoxyethylacetic acid.

*Glycol Monophenyl Ether*,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ .

To obtain this substance, sodium (1 atom) was dissolved in ethylic alcohol, phenol (1 mol.) and glycol chlorhydrin (1 mol.) added, and the mixture heated in a reflux apparatus until neutral. The alcohol was then distilled off, water added, and the product extracted with ether. After washing well, first several times with dilute caustic soda to remove phenol, and afterwards with water, the ethereal solution was evaporated, and the residue distilled under diminished pressure; the whole distilled between  $163^\circ$  and  $166^\circ$  (80 mm. pressure), the yield being very good. A portion boiling at  $165^\circ$  was collected for analysis, and gave the following numbers.

0.1316 gave 0.0864  $\text{H}_2\text{O}$  and 0.3358  $\text{CO}_2$ .  $\text{C} = 69.59$ ;  $\text{H} = 7.28$ .

$\text{C}_8\text{H}_{10}\text{O}_2$  requires  $\text{C} = 69.56$ ;  $\text{H} = 7.24$  per cent.

This ether is a colourless, thick, oily liquid, insoluble in water, but readily soluble in ether or alcohol.

*$\beta$ -Chlorethyl Phenyl Ether*,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ .

This has already been obtained by Henry (*Bull. Soc. Chim.*, 1883, 40, 323) by treating potassium phenoxide with ethylene chlorobromide; in preparing large quantities of this compound we operated as follows.

To an alcoholic solution of sodium phenoxide (1 mol.) ethylene chlorobromide (1 mol.) was added, and the mixture heated on the water bath in a reflux apparatus; sodium bromide immediately began to separate, and after about two hours boiling the mixture was neutral. The alcohol was now distilled off, water added, and the product extracted with ether; the ethereal solution, washed with caustic soda to remove phenol, and afterwards with water, was dried over calcium chloride, evaporated, and the residue distilled. The chief portion boiled between  $210$  and  $230^\circ$ , but there was a considerable residue, which solidified after a time, and consisted of ethylene diphenyl ether (see p. 166); on redistilling the fraction  $210$ — $230^\circ$ , it was found that it boiled at  $220^\circ$ , and on standing some time nearly the whole of the distillate solidified to a beautiful white, crystalline mass, melting at  $28^\circ$ .

0.2501 gave 0.2305  $\text{AgCl}$ .  $\text{Cl} = 22.8$ .

$\text{C}_8\text{H}_9\text{OCl}$  requires  $\text{Cl} = 22.75$  per cent.

The crystals are very readily soluble in light petroleum, benzene, and alcohol. Henry (*loc. cit.*) gives the melting and boiling points of this substance at  $25^\circ$  and  $221^\circ$  (754 mm.) respectively.

*$\beta$ -Bromethyl Phenyl Ether*,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ .

This substance is prepared in a manner exactly similar to the chlorinated derivative, using ethylene dibromide in place of ethylene chlorobromide. During the operation, large quantities of vinylic bromide, formed from the ethylene dibromide by the removal of hydrogen bromide by the sodium phenoxide, issue from the condenser, and, owing to this secondary action, large quantities of unchanged phenol are found in the product; as this interferes considerably with the fractionation of the product if it is not entirely removed, care must be taken to wash the ethereal solution repeatedly with dilute soda, until it is quite free from phenol. The product is then fractionated under diminished pressure, as the bromide decomposes if distilled under the ordinary pressure. The fraction distilling at

140—150° (at 40 mm.) is collected; the residue which solidifies is described later. On redistillation, the bromide boiled almost constantly at 144° (at 40 mm.), and gave the following numbers on analysis.

0.2124 gave 0.1991 AgBr. Br = 39.89.

$C_8H_9OBr$  requires Br = 39.8 per cent.

*β*-Bromomethyl phenyl ether is a white, crystalline substance, melting at 35°. It possesses in a very high degree the property of superfusion, a pure sample having been kept liquid in a bottle for several weeks; on removing the stopper the whole solidified with considerable evolution of heat. The yield of bromide obtained by the above method is about 20 per cent. of the theoretical.

*β*-Bromomethyl phenyl ether was first prepared by Weddige (*J. pr. Chem.*, 1881, [2], 24, 242), by the action of ethylene bromide on sodium phenoxide, but the details of the preparation and purification as given by him are troublesome; after many experiments the above method of procedure was found to be the most convenient. According to Weddige, the ether melts at 39°, and distils at 240—250°, undergoing decomposition and evolving hydrogen bromide.

*Ethylene Diphenyl Ether*,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OC_6H_5$ .

The residue left after distillation of the *β*-brom- (or *β*-chlor-) ethyl phenyl ether solidifies to an almost colourless crystalline mass, which can be readily crystallised from light petroleum (b. p. 100—120°), in which it is easily soluble on boiling, but almost insoluble in the cold. After repeated recrystallisation, the product melted at 96°, and gave the following numbers on analysis.

0.1402 gave 0.4025  $CO_2$  and 0.0828  $H_2O$ . C = 78.29; H = 6.56.

$C_{14}H_{14}O_2$  requires C = 78.5; H = 6.54 per cent.

Burr (*Zeit. für Chem.*, 1869, 165), who first prepared this substance, gives the melting point as 98.5°, whereas Lipmann (*Zeit. für Chem.*, 1869, 447) states that it melts at 95°.

*Action of Methylene Chloride and Methylene Iodide on Sodium Phenoxide.*

*Methylene Diphenyl Ether*,  $C_6H_5 \cdot O \cdot CH_2 \cdot O \cdot C_6H_5$ .

These experiments were instituted in the hope of obtaining chloromethyl phenyl ether and iodomethyl phenyl ether, substances which were required for a series of synthetical experiments.

Methylene iodide,  $CH_2I_2$ , and methylene chloride,  $CH_2Cl_2$ , were treated with sodium phenoxide, in proportions theoretically required to form  $C_6H_5 \cdot O \cdot CH_2I$  and  $C_6H_5 \cdot O \cdot CH_2Cl$ . In the former case, the



mixture was heated on the water bath in a reflux apparatus, but when the chloride was used the mixture was heated in soda-water bottles in boiling water for five hours; the product was isolated exactly as described in the case of the preparation of  $\beta$ -bromomethyl phenyl ether from ethylene dibromide. In the present case, however, the sodium phenoxide, curiously enough, acts on one half of the iodide or chloride only, and leaves the other half unchanged; methylene diphenyl ether being the sole product of the action. This compound is a colourless, syrupy liquid boiling at  $205^{\circ}$ , under a pressure of 50 mm. When cooled to  $0^{\circ}$  it solidifies to a colourless, crystalline mass, which melts at about  $15^{\circ}$ . The following numbers were obtained on analysis.

0.1187 gave 0.3377  $\text{CO}_2$  and 0.0715  $\text{H}_2\text{O}$ . C = 77.59; H = 6.69.

0.1523 „ 0.4334 „ „ 0.0810 „ C = 77.61; H = 5.91.

$\text{C}_{13}\text{H}_{12}\text{O}_2$  requires C = 78.00; H = 6.00 per cent.

Attempts were subsequently made to obtain  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\text{Br}$  from the compound just described by treating it with hydrogen bromide under various conditions, but in this we were unsuccessful, as, even when we used the theoretical quantity of hydrogen bromide dissolved in acetic acid, one-half was converted into methylene dibromide and the other half remained unchanged.

Methylene diphenyl ether has been described by Henry (*Ann. Chim. Phys.*, 1883, [5], 30, 269) and by Arnhold (*Annalen*, 1887, 240, 201) as a liquid boiling at  $293$ – $295^{\circ}$ .

*$\gamma$ -Phenoxyethylmalonic acid*,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{COOH})_2$ .

This substance is easily prepared as follows:—Ethylic malonate (13 grams) is added to sodium (2 grams) dissolved in alcohol (25 grams), and the mixture treated with  $\beta$ -bromomethyl phenyl ether (14 grams). The whole is then heated on the water bath in a reflux apparatus till neutral, after which it is cooled, diluted with water, and the oil which separates extracted with ether; the ether is evaporated, and the light yellow, oily residue hydrolysed by boiling with alcoholic potash (14 grams) for two hours. The alkaline solution is evaporated with water until all the alcohol has been expelled, and is then acidified and extracted with ether; the ethereal solution is dried over calcium chloride, the ether boiled off, and the resulting oil poured into a basin when it quickly solidifies. Finally the substance is purified by crystallisation from xylene from which it separates in minute needles melting at about  $142^{\circ}$  with slight evolution of gas.

Analyses.

0.1168 gave 0.2520  $\text{CO}_2$  and 0.0586  $\text{H}_2\text{O}$ . C = 58.84; H = 5.39.

$\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{COOH})_2$  requires C = 58.93; H = 5.35.



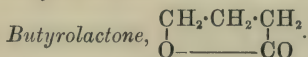
*γ-Phenoxyethylmalonic acid* is sparingly soluble in cold, readily in hot water; it is very sparingly soluble in benzene, and almost insoluble in light petroleum, but it dissolves very easily in alcohol and ethylic acetate, and is fairly soluble in ether.

*γ-Phenoxybutyric acid (γ-Phenoxyethylacetic acid),*  
 $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}.$

This acid was readily obtained on heating *γ*-phenoxyethylmalonic acid at 150—160° until the rapid evolution of carbon dioxide had slackened, and then finally raising the temperature to 200° for a few minutes; the residual syrup, which was of a pale brownish colour, solidified to a hard mass on cooling. It was easily purified by recrystallisation from light petroleum (b. p. 100—120°), from which it separates in thin plates melting at 64—65°.

0.1346 gave 0.3282  $\text{CO}_2$  and 0.0808  $\text{H}_2\text{O}$ .  $\text{C} = 66.50$ ;  $\text{H} = 6.67$ .  
 $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$  requires  $\text{C} = 66.66$ ;  $\text{H} = 6.66$  per cent.

*γ-Phenoxybutyric acid* is sparingly soluble in cold water, easily in hot, and, on cooling, separates in the flocculent condition. It is easily soluble in benzene, ethylic acetate, alcohol, and acetic acid.



A number of experiments were conducted with the object of discovering the best possible means of replacing the phenoxy-group in *γ*-phenoxybutyric acid by the hydroxy-group; in this case the *γ*-hydroxybutyric acid formed would immediately lose water, yielding butyrolactone.

The following method gave the best results. *γ*-Phenoxybutyric acid (25 grams) was gently heated on the water bath with fuming hydrobromic acid (60 c.c.) in a reflux apparatus for about eight hours, and afterwards for the same length of time on the sand bath. On cooling and diluting with water, a heavy black oil separated which was extracted with pure ether, and the ethereal solution washed with water. The ethereal solution was then extracted several times with a strong solution of sodium carbonate, the extracts boiled with animal charcoal for 12 hours, and the liquid filtered from the animal charcoal; the pink filtrate, after being evaporated to a small bulk, was extracted with ether to remove phenol, and then acidified and again extracted repeatedly with pure ether. This ethereal solution was dried over calcium chloride, the ether removed by evaporation, and the residual oil (about 5 grams) fractionated. Practically the whole of the oil distilled between 204° and 206° at the atmospheric pressure, and a sample of the oil boiling at 205° yielded the following results on analysis.

0.1020 gave 0.2090  $\text{CO}_2$  and 0.0646  $\text{H}_2\text{O}$ .  $\text{C} = 55.88$ ;  $\text{H} = 7.03$ .

$\text{C}_6\text{H}_5\text{O}_2$  requires  $\text{C} = 55.81$ ;  $\text{H} = 6.97$  per cent.

The substance was, therefore, evidently  $\gamma$ -butyrolactone, which, according to Fittig and Roeder (*Annalen*, 1885, **227**, 22), boils at  $206^\circ$ .

*Diphenoxyethylmalonic acid*,  $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{C}(\text{COOH})_2$ .

This acid has been prepared in considerable quantities; the method we usually employed being as follows:—Ethylic malonate (16 grams) is added to sodium (2.3 grams), dissolved in alcohol (30 grams), and the mixture heated with  $\beta$ -bromethyl phenyl ether (20 grams) on the water bath till neutral; the product is then cooled and again treated with sodium (2.3 grams), dissolved in alcohol (30 grams), and  $\beta$ -bromethyl phenyl ether (20 grams), and the mixture once more heated on the water bath till neutral. On adding water, a heavy oil separates; this is extracted with ether, the ether removed by evaporation, and the oily residue hydrolysed by boiling with alcoholic potash (17 grams). After removing the alcohol by evaporation with water, the solution is acidified, and the copious white precipitate of crude diphenoxyethylmalonic acid thus produced is collected, washed with water, and dried on a porous plate until quite free from oily impurity. It is then purified by recrystallisation from 50 per cent. acetic acid from which it separates in rhombic prisms melting and decomposing at  $150^\circ$ .

0.1266 gave 0.3098  $\text{CO}_2$  and 0.0680  $\text{H}_2\text{O}$ .  $\text{C} = 66.44$ ;  $\text{H} = 5.96$ .  
 $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{C}(\text{COOH})_2$  requires  $\text{C} = 66.28$ ;  $\text{H} = 5.81$  per cent.

*Diphenoxyethylmalonic acid* is almost insoluble in cold water, very slightly soluble in hot water or benzene, and almost insoluble in light petroleum; it is moderately soluble in ether, ethylic acetate, and alcohol, and is extremely soluble in acetic acid. It is reprecipitated by water from its alcoholic and acetic acid solutions.

*Diphenoxyethylacetic acid*,  $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH}$ .

This compound was prepared by heating diphenoxyethylmalonic acid at  $180^\circ$  until carbon dioxide ceased to be evolved; the brown, syrupy residue solidified completely on cooling, and was readily purified by recrystallisation from light petroleum (b. p.  $100$ – $120^\circ$ ), from which it separated in feathery groups, melting at  $88^\circ$ .

0.1054 gave 0.2788  $\text{CO}_2$  and 0.0625  $\text{H}_2\text{O}$ .  $\text{C} = 72.14$ ;  $\text{H} = 6.59$ .  
 $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH}$  requires  $\text{C} = 72.00$ ;  $\text{H} = 6.66$  per cent.

*Diphenoxyethylacetic acid* is insoluble in cold, and only sparingly soluble in hot, water; it is sparingly soluble in cold, light petroleum,

easily in the hot liquid, and very soluble in benzene, ethylic acetate, alcohol, and acetic acid; its alcoholic and acetic acid solutions yield flocculent precipitates when diluted with water.

*β-Phenoxyethyl-γ-hydroxybutyric acid*,  $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2 > \text{CH}\cdot\text{COOH}$ .

This substance was obtained accidentally in examining the product formed by heating a sample of crude diphenoxyethylacetic acid in a sealed tube with a solution of hydrogen chloride in acetic acid for some hours at about  $130^\circ$ ; the contents of the tube were diluted with water, and the dark, heavy oil which was precipitated was extracted with ether, the ethereal solution washed repeatedly with water to remove acetic acid, and the ether evaporated. The dark, oily residue was then boiled with a strong solution of sodium carbonate for a considerable length of time, in order to remove chlorine. The alkaline solution was now extracted with ether, to remove phenol, acidified, extracted with ether, and the ethereal solution dried with calcium chloride and filtered; shortly afterwards it was observed that crystals were separating from the ethereal solution; these were collected, washed with ether, dried on a porous plate, and recrystallised twice from benzene, in which it dissolves but slightly. It crystallises in prisms, which melt at  $112^\circ$ , but sinter several degrees below this temperature.

0.1083 gave 0.2578  $\text{CO}_2$  and 0.0716  $\text{H}_2\text{O}$ .  $\text{C} = 64.92$ ;  $\text{H} = 7.35$ .

$\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2 > \text{CH}\cdot\text{COOH}$  requires  $\text{C} = 64.28$ ;  $\text{H} = 7.14$  per cent.

When pure, this substance is almost insoluble in ether, very sparingly soluble in light petroleum, but moderately easily in water.

The *silver salt*,  $\text{C}_{12}\text{H}_{15}\text{AgO}_4$ , was prepared by precipitating an aqueous solution of the ammonium salt with silver nitrate; it is moderately soluble in hot water, and crystallises on cooling in white tufts.

0.1092 gave 0.0358 Ag.  $\text{Ag} = 32.78$ .

$\text{C}_{12}\text{H}_{15}\text{AgO}_4$  requires  $\text{Ag} = 32.63$  per cent.

With copper sulphate solution, the aqueous solution of the ammonium salt gives a bluish-white precipitate, which dissolves on boiling, and separates out again on cooling, apparently not in the crystalline condition.

Lead acetate solution gives no precipitate at first, but, on standing, a white, crystalline salt gradually separates; this redissolves on boiling, and crystallises out again on cooling.

Barium nitrate and calcium chloride give no precipitate with the aqueous solution of the ammonium salt.



*Action of  $\beta$ -Bromethyl Phenyl Ether on the Sodium Derivative of Ethylic Methylmalonate.*

*Ethylic  $\gamma$ -Phenoxyethyl- $\alpha$ -Methylmalonate,*  
 $C_6H_5O \cdot CH_2 \cdot CH_2 \cdot C(CH_3)(COOC_2H_5)_2$ .

This substance is obtained when the bromo- or chloro-ether,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Br$  or  $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Cl$  (1 mol.), reacts with the sodium derivative of ethylic methylmalonate (1 mol.) in alcoholic solution. In the case of the chloride, the action proceeds slowly, six hours boiling being required to complete it, but in the case of the bromide, it sets in on gently warming, and is so vigorous as to maintain the mixture at the boiling point for some time; when the decomposition is complete, water is added, and the oily product is extracted with ether. The ethereal solution is washed with water, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure, when the bulk of it distils at  $230^\circ$  (45 mm.) as a colourless, thick oil, which, on analysis, gave the following numbers.

0.1392 gave 0.0927  $H_2O$  and 0.3318  $CO_2$ .  $C = 65.01$ ;  $H = 7.39$ .

$C_{16}H_{22}O_5$  requires  $C = 65.3$ ;  $H = 7.48$  per cent.

*Ethylic  $\gamma$ -phenoxyethyl- $\alpha$ -methylmalonate* is a colourless syrup, which, even on long standing, showed no signs of crystallising.

During the fractionation of the crude product of the action of phenoxyethylbromide on ethylic sodiomethylmalonate, a considerable quantity of an oil of low boiling point was obtained, which, on subsequent fractionation under the ordinary pressure, was found to contain, besides ethylic methylmalonate, a liquid free from halogen, and boiling at about  $230^\circ$ . In order to free this substance from ethylic methylmalonate, it was boiled with excess of alcoholic potash for four or five hours, when a large quantity remained unsaponified. Water was added, the oil which was precipitated extracted with ether, the ethereal solution well washed with water, dried, and evaporated. The oily residue thus obtained, when distilled, boiled constantly at  $230^\circ$  under the ordinary pressure. The analytical results agreed with the formula  $C_6H_5O \cdot CH_2 \cdot CH_2 \cdot OC_2H_5$ .

0.1502 gave 0.1150  $H_2O$  and 0.3974  $CO_2$ .  $C = 72.15$ ;  $H = 8.50$ .

$C_{10}H_{14}O_2$  requires  $C = 72.28$ ;  $H = 8.43$  per cent.

*$\beta$ -Ethoxyethyl phenyl ether* is a colourless, mobile oil of penetrating odour, resembling that of benzyl ethyl ether,  $C_6H_5 \cdot CH_2 \cdot OC_2H_5$ .

*$\gamma$ -Phenoxyethyl- $\alpha$ -methylmalonic acid,*  
 $C_6H_5O \cdot CH_2 \cdot CH_2 \cdot C(CH_3)(COOH)_2$ .

In order to prepare this acid, ethylic  $\gamma$ -phenoxyethyl- $\alpha$ -methylmalonate (50 grams) was boiled with alcoholic potash (50 grams).



There appeared to be very little action in the cold, but, on gently warming, a large quantity of an insoluble potassium salt soon separated; sufficient water was added to dissolve nearly the whole of this, and the mixture boiled on the water bath in a reflux apparatus for two or three hours. Water was then added, the alcohol completely removed by evaporation on the water bath, the residue dissolved in water, cooled, and acidified with hydrochloric acid; the crude  $\gamma$ -phenoxyethyl- $\alpha$ -methylmalonic acid, which then separated as a thick, heavy, brown oil, was extracted with pure ether, and the ethereal solution dried over calcium chloride and evaporated. After standing overnight in a vacuum over sulphuric acid, the oil solidified to a hard crystalline mass, which was readily purified by recrystallisation from hot benzene. The following are the results of the analysis of this substance.

0.1312 gave 0.0684  $\text{H}_2\text{O}$  and 0.2920  $\text{CO}_2$ .  $\text{C} = 60.69$ ;  $\text{H} = 5.79$ .

$\text{C}_{12}\text{H}_{14}\text{O}_5$  requires  $\text{C} = 60.50$ ;  $\text{H} = 5.88$  per cent.

*$\gamma$ -Phenoxyethyl- $\alpha$ -methylmalonic acid* crystallises in colourless prisms which melt at  $125^\circ$  with decomposition and formation of  $\gamma$ -phenoxyethyl- $\alpha$ -methylacetic acid and carbon dioxide. It is sparingly soluble in cold water or cold benzene, and insoluble in light petroleum, but readily soluble in hot water, hot benzene, alcohol, or ether.

*$\gamma$ -Phenoxyethyl- $\alpha$ -methylacetic acid*,  $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ .

This substance was prepared by heating  $\gamma$ -phenoxyethyl- $\alpha$ -methylmalonic acid at  $180^\circ$  until evolution of carbon dioxide had entirely ceased, and then distilling the residual oil under diminished pressure. The whole distilled between  $205^\circ$  and  $210^\circ$  (45 mm.), the correct boiling point at this pressure being  $207^\circ$ . A small portion of the distillate, which, on cooling, solidified immediately, was recrystallised from light petroleum ( $60\text{--}90^\circ$ ), and thus obtained in the form of small, colourless crystals melting at  $80^\circ$ .

0.1745 gave 0.1100  $\text{H}_2\text{O}$  and 0.4345  $\text{CO}_2$ .  $\text{C} = 67.91$ ;  $\text{H} = 7.00$ .

$\text{C}_{11}\text{H}_{14}\text{O}_3$  requires  $\text{C} = 68.04$ ;  $\text{H} = 7.21$  per cent.

This acid is readily soluble in alcohol, ether, or benzene, moderately so in hot water and light petroleum, but only sparingly in the two last-named solvents in the cold.

*Silver salt*,  $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOAg}$ .—This was prepared by suspending the acid in water and gradually adding ammonia until the whole had dissolved; the solution was then boiled to get rid of the slight excess of ammonia, and silver nitrate added when the solution was cold. The white, flocculent precipitate thus obtained was collected, washed well with water, spread on a porous plate, and dried in a vacuum over sulphuric acid.

0.0910 gave 0.0382 H<sub>2</sub>O and 0.1456 CO<sub>2</sub>. C = 43.65; H = 4.66.

0.1298 „ 0.0467 Ag. Ag = 35.98.

C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>Ag requires C = 43.85; H = 4.32; Ag = 35.88 per cent.

This silver salt is somewhat soluble in boiling water, and separates again, in the amorphous condition, on cooling. A neutral solution of the ammonium salt of  $\gamma$ -phenoxyethyl- $\alpha$ -methylacetic acid gives no precipitate with barium or calcium salts, but, on adding lead acetate, a white, amorphous precipitate is thrown down, which is somewhat soluble in boiling water. With copper sulphate a flocculent green precipitate is obtained insoluble in boiling water.

*Action of Bromethyl Phenyl Ether on Ethylic Methylacetoacetate.*

This reaction was carried out as follows. Sodium (4 grams) was dissolved in ethylic alcohol (50 grams), the solution cooled, and a mixture of ethylic methylacetoacetate (25 grams) and bromethyl phenyl ether (35 grams) added. In the cold there appeared to be no action, but, on heating on the water bath in a reflux apparatus, sodium bromide quickly separated; the mixture, which, after boiling for about two hours was neutral, was poured into water, and the oily products extracted with ether in the usual way. On distilling the dry product under a pressure of 40 mm. ethylic methylacetoacetate first passed over; the thermometer then rose rapidly, and at 185° almost the whole of the new compound distilled.

0.1400 gave 0.0983 H<sub>2</sub>O and 0.3473 CO<sub>2</sub>. C = 67.64; H = 7.80.

C<sub>6</sub>H<sub>5</sub>O·[CH<sub>2</sub>]<sub>2</sub>·C(CH<sub>3</sub>)(CO·CH<sub>3</sub>)·COOC<sub>2</sub>H<sub>5</sub> requires C = 68.10; H = 7.58 per cent.

Ethylic  $\gamma$ -phenoxyethyl- $\alpha$ -methylacetoacetate is a thick, colourless oil which, on hydrolysis with strong alcoholic potash, yields  $\gamma$ -phenoxyethyl- $\alpha$ -methylacetic acid.

*Formation of  $\alpha$ -Methylbutyrolactone from  $\gamma$ -Phenoxyethyl- $\alpha$ -methylacetic acid.*

$\gamma$ -Phenoxyethyl- $\alpha$ -methylacetic acid is moderately easily decomposed by heating with mineral acids with formation of  $\alpha$ -methylbutyrolactone; the best results being obtained as follows. The pure acid is heated in sealed tubes with a strong solution of hydrogen bromide in glacial acetic acid for six hours at 100°; the contents of the tubes are then diluted with water, the products extracted with ether, and after the ethereal extract has been washed with water until free from acetic acid, the ether is distilled off, and the residue is boiled with potassium carbonate solution for 12 hours. The phenol formed is then removed by means of ether, the aqueous solution concentrated on the water bath, and, after cooling, acidified and boiled in a reflux

apparatus for two hours, to convert the hydroxy-acid into the lactone. The solution is then repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, evaporated, and the product distilled. In this way, a colourless, mobile liquid is obtained which boils constantly at  $201^{\circ}$ , and is evidently identical with the  $\alpha$ -methylbutyrolactone described by Marburg (*Ber.*, 1895, **28**, 10).

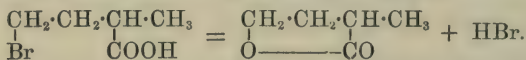
*$\alpha$ -Methyl- $\gamma$ -bromobutyric acid.*

In order to prepare this substance, pure  $\alpha$ -methylbutyrolactone is left for 24 hours at the ordinary temperature in contact with saturated aqueous hydrobromic acid; the product is poured into water, all rise of temperature being carefully avoided, and the liquid rapidly extracted with ether. After washing well with water, the ethereal solution is dried and evaporated, when a brown, oily residue is left, which cannot be purified by distillation, as it decomposes readily on warming; for analysis it was, therefore, merely left over sulphuric acid in a vacuum for a short time.

0.2732 gave 0.2840 AgBr. Br = 44.04.

$C_5H_9BrO_2$  requires Br = 44.19 per cent.

This acid gives off hydrogen bromide at ordinary temperatures, very probably with formation of  $\alpha$ -methylbutyrolactone.



*Ethyl  $\gamma$ -Brom- $\alpha$ -methylbutyrate*,  $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOC}_2\text{H}_5$ .—The impure  $\gamma$ -brom- $\alpha$ -methylbutyric acid obtained as described above was dissolved in ethylic alcohol and the solution saturated with dry hydrogen chloride; after 24 hours, water was added, the ethereal salt extracted with ether, and the ethereal solution, after being well washed with water and sodium carbonate solution, was dried over calcium chloride, and evaporated. In this case also, the oily residue could not be distilled, for although it did not give off hydrogen bromide so readily in the cold as the acid did, it decomposed rapidly below its boiling point. After standing in a vacuum over sulphuric acid for 12 hours, the bromine was determined.

0.2460 gave 0.2146 AgBr. Br = 37.12.

$C_7H_{13}O_2Br$  requires Br = 38.27 per cent.

*Action of Phosphorus Pentachloride on  $\alpha$ -Methylbutyrolactone.*

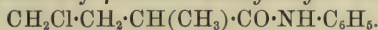
In order to study this decomposition, phosphorus pentachloride (20 grams) was gradually added to  $\alpha$ -methylbutyrolactone (10 grams), the mixture being well cooled with water during the addition. When all the pentachloride had been added, and the whole

allowed to stand for one hour, the action was completed by heating for one hour on the water bath. On subsequently distilling the product, phosphorus oxychloride passed over first, and then the temperature rose to  $189^{\circ}$ , at which the rest distilled; there was, however, some decomposition accompanied by charring and evolution of hydrogen chloride. The analysis of the product obtained in this way did not give very good analytical results, although they indicated that the substance was  $\gamma$ -chlor- $\alpha$ -methylbutyryl chloride,



this was borne out by the study of the properties of the chloride.

*Anilide of  $\gamma$ -Chlor- $\alpha$ -methylbutyric acid,*



This crystalline substance is obtained when the product of the action of phosphorus pentachloride on  $\alpha$ -methylbutyrolactone is slowly poured into aniline, the mixture being well cooled during the addition. After standing for one hour, the product is poured into water, dilute hydrochloric acid added until the excess of aniline has been removed, and the whole extracted with ether. The ethereal solution, after being washed successively with dilute hydrochloric acid and with water, is evaporated, and the residue left in a vacuum over sulphuric acid until it gradually deposits crystals. These are freed from oily mother liquor on a porous plate, and then recrystallised from light petroleum (b. p.  $100$ — $120^{\circ}$ ). The beautiful white prisms thus obtained melt at  $106^{\circ}$ .

0.1155 gave 7.0 c.c. moist nitrogen at  $18^{\circ}$  and 753 mm.  $\text{N} = 6.96$ .

$\text{C}_{11}\text{H}_{14}\text{OClN}$  requires  $\text{N} = 6.62$  per cent.

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THE SYMMETRICAL DIMETHYLSUCCINIC  
ACIDS.

BY

WILLIAM ARTHUR BONE

AND

WILLIAM HENRY PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1896.]



## The symmetrical dimethylsuccinic acids.

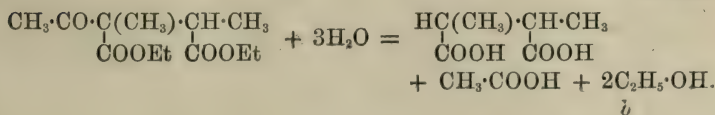
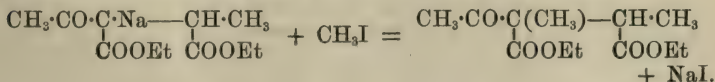
By WILLIAM ARTHUR BONE, and WILLIAM HENRY PERKIN, Jun.

### INTRODUCTION.

IN 1869, Wislicenus (*Ber.*, 1869, **2**, 720) described as dimethylsuccinic acid a substance which he had observed among the products of the reduction of iodopropionic acid by means of zinc dust. The substance itself was a syrup, which only partially crystallised on long standing, but it yielded a highly characteristic lead salt, which, on analysis, gave results corresponding with the empirical formula  $C_6H_8PbO_4$ .

Five years later, Weidel (*Annalen*, 1874, **173**, 109), by the reduction of pyrocinchonic acid,  $\begin{array}{c} CH_3 \cdot C \cdot CO \\ || \\ CH_3 \cdot C \cdot CO \end{array} > O$ , by means of sodium amalgam, obtained a crystalline acid, melting at  $170^\circ$ , which could be sublimed, for the most part without change, and which he termed "hydropyrocinchonic acid."

In 1878, v. Hardtmuth (*Annalen*, **192**, 142), working under the direction of Wislicenus, studied the action of methylic iodide on the sodium compound of ethylic  $\beta$ -methylacetosuccinate in benzene solution, and on hydrolysing, by means of alcoholic potash, the ethereal salt thus formed, obtained a "dimethylsuccinic acid" melting at  $170^\circ$ . The reactions involved in this process may be thus written





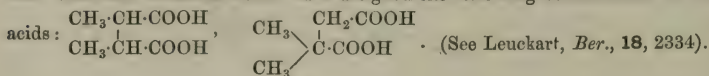
In 1882, v. Roser (*Ber.*, **15**, 2012) obtained "hydropyrocinchonic acid" by the reduction of pyrocinchonic acid by means of hydrogen iodide, and found that it melted at  $190^{\circ}$ . A very similar result was obtained by Weidel and Brix (*Monatsh.*, 1882, **3**, 612), who, however, used sodium amalgam as the reducing agent; the acid they obtained crystallised in glistening, triclinic needles, melting at  $189^{\circ}$ .

Three years later, Otto and Beckurts (*Ber.*, 1885, **18**, 825) published the results of a detailed investigation on the reduction of pyrocinchonic acid. When this acid was reduced by hydrogen iodide in sealed tubes at  $220^{\circ}$ , two acids were obtained, which could easily be separated by fractional crystallisation from water; the more insoluble acid melted at  $193\text{--}194^{\circ}$ , and seemed to be identical with the acids obtained by v. Roser and Weidel and Brix respectively, whilst the other melted at  $118\text{--}120^{\circ}$ . Quite different results were obtained when sodium amalgam was used as the reducing agent; in this case, in addition to the acid melting at  $193\text{--}194^{\circ}$ , there was produced an isomeric acid which melted without decomposition at  $240\text{--}241^{\circ}$ , whilst the acid melting at  $118\text{--}120^{\circ}$  was not to be found among the products of reduction. This last experiment gave results, therefore, quite different from that in which hydrogen iodide was employed as the reducing agent, but, on repeating it, no trace of the acid melting at  $240\text{--}241^{\circ}$  could be detected amongst the products, which, on the other hand, contained acids melting at  $193\text{--}194^{\circ}$  and  $118\text{--}120^{\circ}$ .

An examination of the acid melting at  $193\text{--}194^{\circ}$  showed that when it was heated to  $200^{\circ}$  it was transformed into an anhydride melting at  $186\text{--}187^{\circ}$ , which dissolved in hot water, and yielded, not the original acid, but the acid melting at  $240\text{--}241^{\circ}$ , which they found might be distilled without decomposition. They concluded, therefore, that these acids stood to one another in the same relationship as do fumaric and maleic acids, and they termed them dimethylsuccinic and isodimethylsuccinic acids respectively.\*

They found that when the acid melting at  $118\text{--}120^{\circ}$  was heated to  $160^{\circ}$ , it decomposed with evolution of carbonic anhydride, and concluded that it was identical with the ethylmethylmalonic acid prepared in 1880 by Conrad and Bischoff (*Annalen*, **204**, 143, 162), which melt at  $118^{\circ}$ .

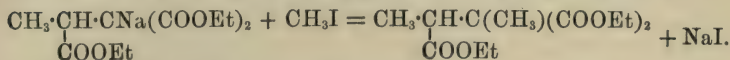
\* Otto and Beckurts published their paper in 1885, two years before Wislicenus put forward his views as to the constitution of fumaric and maleic acids. From the views then held as to the constitution of the last-named acids, we may infer that Otto and Beckurts would have assigned the following constitutions to their



M. p.  $193\text{--}194^{\circ}$ .      M. p.  $240\text{--}241^{\circ}$ .

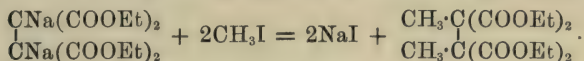
In 1886, Bischoff and Rasch (*Annalen*, **234**, 54) prepared a symmetrical dimethylsuccinic acid synthetically by three methods, which may be briefly described as follows.

1. By the action of methylic iodide on the sodium derivative of ethylic propenyltricarboxylate, according to the equation



The oil formed was hydrolysed by means of alcoholic potash, and the tricarboxylic acid thus obtained was heated at 160° until the evolution of gas had entirely ceased.

2. By hydrolysis of ethylic dimethylacetosuccinate (prepared by the action of ethylic  $\alpha$ -bromopropionate on the sodium derivative of ethylic methylacetoacetate) by means of alcoholic potash.
3. By the action of methylic iodide on the disodium derivative of ethylic acetylenetetracarboxylate, according to the equation



The oil formed was hydrolysed by means of potassium hydroxide, and the tetracarboxylic acid obtained was heated at 170° until the evolution of gas had entirely ceased.

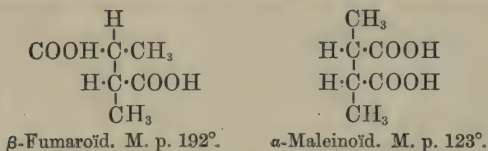
They found that the dimethylsuccinic acid obtained by either of these methods melted at 187°, and that on being heated to its melting point it lost water, and yielded an anhydride melting at 87°.

These results were fully confirmed by Leuckhart (*Ber.*, 1885, **18**, 2344), who prepared the acid synthetically from ethylic methylmalonate and ethylic  $\alpha$ -bromopropionate. He found that it melted at 188—189°, and at that temperature was converted into an anhydride melting at 78—81°, which, with hot water, yielded, besides the original acid melting at 189°, an isomeride melting at 121—122°. The last-named acid, although it resembled in some respects, such as crystalline form and solubility, the acid melting at 118—120°, obtained by Otto and Beckurts by the reduction of pyrocinchonic acid, differed from it in that it might be distilled apparently without change. It will be observed that Leuckhart's results were quite incompatible with those of Otto and Beckurts; matters were, however, considerably cleared up in the following year, when Otto and Rössing published a remarkable paper (*Ber.*, 1887, **20**, 2737), which contained an entire refutation of the conclusions arrived at by Otto and Beckurts two years previously. They now found that their dimethylsuccinic acid melting at 193—194° is *not* changed, on heating to 200°, into an

anhydride melting at 186—187°, which with water yields “isodimethylsuccinic acid” melting at 240—241°, but, on the contrary, like Bischoff’s dimethylsuccinic acid, it was converted into an anhydride melting at 86—87°, which with water yielded the original acid again. The acid, when treated with acetyl chloride, was converted into a mixture of two anhydrides, one of which melted at 86°, and the other at 38°, the last-named, with water, again yielding the original acid melting at 195°.

Further, they found that the acid melting at 121°, which Otto and Beckurts had obtained by the reduction of pyrocinchonic acid, did not decompose at 180° with evolution of carbonic anhydride, and, therefore, could no longer be considered as ethylmethylmalonic acid; on the contrary, it was converted by acetyl chloride into an anhydride melting at 87°, which with water yielded a mixture of two acids melting at 195° and 121° respectively. They concluded, therefore, that both these acids were dimethylsuccinic acids.

In 1888, Zelinsky (*Ber.*, 1888, **21**, 3160) prepared two symmetrical dimethylsuccinic acids by the hydrolysis of  $\alpha\alpha$ -dimethylecyanosuccinate (obtained by the action of potassium cyanide on ethylic  $\alpha$ -bromopropionate) by means of concentrated hydrochloric acid. One acid melted at 192°, and was almost insoluble in cold water; the other melted at 123—124°, and was fairly soluble in water. Both acids, on distillation, were transformed into the same anhydride, melting at 87°, which dissolved in water yielding the lower melting acid. He proposed the following constitutional formulæ for these acids:—



In 1890, Bischoff and Voit (*Ber.*, 1890, **23**, 639) reinvestigated these acids, their results in the main confirming those of Zelinsky. The two acids melted at 194° (para-acid) and 120° (anti-acid) respectively. At temperatures above 200°, both were converted into the same anhydride melting at 87°; this with water yielded a mixture of the para- and anti-acids. The para-acid, however, when heated with acetyl chloride, was converted into an anhydride melting at 38° (see Otto and Rössing), which with water yielded the para-acid again. On heating the anti-acid with concentrated hydrochloric acid at 180—190°, it was transformed into its isomeride.

In 1893, Crum Brown and Walker (*Annalen*, **274**, 41) prepared the symmetrical dimethylsuccinic acids by the electrolysis of potassium ethylic methylmalonate. They found that the para-acid melted



at  $193^{\circ}$ , and that its dissociation constant was  $K = 0.0208$ , whereas the anti-acid melted at  $120\text{--}121^{\circ}$ , and had the dissociation constant  $K = 0.0138$ .

The results of previous workers are given in tabular form on p. 258.

As the descriptions of the properties of the acids obtained by various experimenters differ so widely, the authors determined to carefully re-investigate the subject, with the results described in this communication.

They have prepared the symmetrical dimethylsuccinic acids in two ways, namely (1), by the hydrolysis of ethylic  $\alpha\alpha$ -dimethylcyanosuccinate with concentrated hydrochloric acid (Zelinsky's method), and (2) by the action of ethylic  $\alpha$ -bromopropionate on the sodium derivative of ethylic methylmalonate, subsequently hydrolysing the product with alcoholic potash, and then heating the tribasic acid thus obtained at  $200^{\circ}$  until the evolution of carbonic anhydride had entirely ceased (Leuckhart's method). In both cases, the authors obtained a mixture of two symmetrical dimethylsuccinic acids, which were separated by fractional crystallisation from water. The melting points of these acids, especially that of the fumaroid (*trans*-) acid, differed materially from those assigned to them by previous investigators. When pure, the fumaroid (*trans*-) acid melts at  $209^{\circ}$ , and with acetyl chloride yields an anhydride melting at  $43^{\circ}$ , which by the action of water is reconverted into the *trans*-acid; it must, therefore, be the anhydride of this acid; further, this anhydride, on prolonged heating with acetic anhydride, is transformed into an isomeric anhydride melting at  $88^{\circ}$ , which, with water, yields the *cis*-acid.

The maleinoid (*cis*-) acid melts at  $129^{\circ}$ , and with acetyl chloride yields an anhydride melting at  $88^{\circ}$ , which with water is reconverted into the original acid, and must, therefore, be the anhydride of the *cis*-acid.

Both acids, when heated for a long time at  $210^{\circ}$ , or on distillation under atmospheric pressure, are converted into the *cis*-anhydride melting at  $88^{\circ}$ . Each of the anhydrides, when pure, yields with water only *one* acid (not a mixture of acids as stated by some previous investigators); that melting at  $43^{\circ}$  yields only the *trans*-acid melting at  $209^{\circ}$ , whilst that melting at  $88^{\circ}$  yields the *cis*-acid melting at  $129^{\circ}$ .

The authors have further shown that the *cis*-acid is almost entirely converted into the *trans*-acid when it is heated with concentrated hydrochloric acid in sealed tubes at  $180^{\circ}$ ; under similar conditions only a very small part of the *trans*-acid is transformed into the *cis*-modification, by far the greater portion of it being recovered unchanged.

Our results may be represented in tabular form as follows (p. 259)



Date.	Investigators and References.	Acids.	m. p. of acids.	Anhydride formation.	m. p. of anhydride.	Anhydride + water.
1869	Wislicenus ( <i>Ber.</i> , <b>2</b> , 720).....	—	Liquid	—	—	—
1874	Weidel ( <i>Annalen</i> , <b>173</b> , 109).....	"Hydropyrocinehonic acid"...	170°	—	—	—
1878	v. Hardtmuth ( <i>Annalen</i> , <b>192</b> , 142)...	"Dimethylsuccinic acid".....	170°	—	—	—
1882	v. Roser ( <i>Ber.</i> , <b>15</b> , 2012).....	"Hydropyrocinehonic acid"...	190°	—	—	—
1882	Weidel and Brix ( <i>Monatsh.</i> , <b>3</b> , 612)...	"Hydropyrocinehonic acid"...	189°	—	—	—
1885	Otto and Beckurts ( <i>Ber.</i> , <b>18</b> , 825).....	"Dimethylsuccinic acid" ... "Isodimethylsuccinic acid" ... "Ethylmethylmalonic acid" ...	193—194° 240—241° 118—120°	Maintained at 200°	186—187°	"Isodimethylsuccinic acid," m. p. = 240—241°.
1885	Leuckhart ( <i>Ber.</i> , <b>18</b> , 2344).....	Dimethylsuccinic acid .....	188—189°	At 200°	79—81°	Mixture of acids, m. p. 189° and 118—120°.
1887	Otto and Rössing ( <i>Ber.</i> , <b>20</b> , 2737)....	Dimethylsuccinic acid .....	193—194° 121°	{ On heating to 200° With acetyl chloride With acetyl chloride	86—87° 38° 87	195° acid. Do. Mixture of acids, m. p. 195° and 121°.
1888	Zelinsky ( <i>Ber.</i> , <b>21</b> , 3160).....	$\alpha$ -maleinoid .....	123° 192°	{ On distillation	87°	Maleinoid acid.
1890	Bischoff and Voit ( <i>Ber.</i> , <b>23</b> , 639).....	Para..... Anti.....	192° 120°	{ At 200° Acetyl chloride At 200°	87° 38 87	Mixture of para- and anti- acids. Para-acid. Mixture of para- and anti- acids.
1893	Crum Brown and Walker ( <i>Annalen</i> , <b>274</b> , 41)	Para..... Anti.....	193° 120—121°	{ —	—	—

Fumaroid (*trans*) acid.Maleinoid (*cis*) acid.

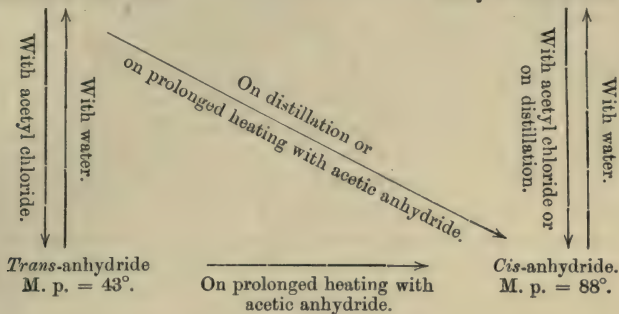
M. p. = 209°.

With conc. HCl at 180°.

M. p. = 129°.

Insoluble in cold water.

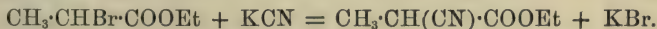
Fairly soluble in cold water.



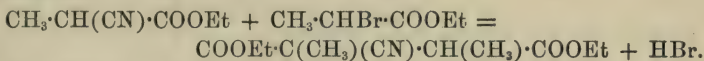
## EXPERIMENTAL PART.

PART I.—A. *Preparation of the Symmetrical Dimethylsuccinic acids from Ethylic  $\alpha$ -Dimethylcyanosuccinate.*

The ethylic  $\alpha$ -dimethylcyanosuccinate used in these experiments was prepared by the action of potassium cyanide on an alcoholic solution of ethylic  $\alpha$ -bromopropionate, according to the method described by the authors in a previous paper (Trans., 1895, **67**, 420). The first action of potassium cyanide on ethylic  $\alpha$ -bromopropionate consists in a replacement of the bromine by the cyanogen group, resulting in the production of ethylic  $\alpha$ -cyanopropionate according to the equation



Subsequently a part of the ethylic  $\alpha$ -cyanopropionate thus formed condenses with some of the unchanged ethylic  $\alpha$ -bromopropionate, the result being the production of *ethylic  $\alpha\alpha$ -dimethylcyanosuccinate*, as follows.



The product, after distilling off the alcohol and extracting with ether in the usual manner, consists of a mixture of unchanged ethylic  $\alpha$ -bromopropionate, ethylic  $\alpha$ -cyanopropionate, and  $\alpha\alpha$ -dimethylcyanosuccinate, which are separated by careful fractionation under reduced pressure (30—40 mm.). The ethylic  $\alpha$ -bromopropionate distils over between 77° and 85°, and the ethylic  $\alpha$ -cyanopropionate between 103° and 110°, whilst the dark-coloured residue in the distilling flask consists for the most part of ethylic  $\alpha\alpha$ -dimethylcyanosuccinate. If the distillation be continued further,

a large quantity of a pale yellow oil passes over between  $170^{\circ}$  and  $200^{\circ}$ ; this oil was twice fractionated under a pressure of 80 mm., and the portion distilling between  $195^{\circ}$  and  $200^{\circ}$  was employed for the preparation of the symmetrical dimethylsuccinic acids.

*Hydrolysis of the Oil.*—The oil was mixed with about five or six times its bulk of concentrated hydrochloric acid in a large, round-bottomed flask, and to the mixture glacial acetic acid was added, until the oil just dissolved. The whole was then heated on a sand bath in a flask fitted with a long glass tube, ground into the neck to serve as a reflux condenser; when a sample of the liquid no longer deposited an oil on being diluted with water, it was allowed to cool, when a large crop of white crystals separated, consisting for the most part of ammonium chloride. The liquid was then poured into a large basin, and evaporated nearly to dryness, first over a bare flame, and finally on a water bath; water was added to the residue, and the solution again evaporated down in the water bath, this time completely to dryness. In this way, all the acetic acid and the ethylic acetate formed during the hydrolysis was got rid of. The residue was finally dissolved in hot water, when, on cooling, the solution deposited a greyish-white, crystalline mass of the crude acids; this was separated from the mother liquor by filtration at the pump, thoroughly washed with cold water, redissolved in hot water, boiled with animal charcoal, and filtered while hot. The filtrate, on standing, deposited a crop of white crystals, which, after drying, melted at  $207\text{--}208^{\circ}$ . After another recrystallisation from hot water, the substance melted at  $209^{\circ}$ . On concentrating the filtrate on the water bath, a further quantity of an acid was obtained on cooling; this acid, separated from the solution by filtration, and recrystallised, also melted at  $209^{\circ}$ . The filtrate was repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off. The thick, oily residue, which solidified on standing, was dissolved in hot benzene; the solution on cooling deposited crystals melting between  $115^{\circ}$  and  $125^{\circ}$ . These were once more crystallised from hot benzene, but no alteration in the melting point occurred; the acid was then dissolved in hot, concentrated, hydrochloric acid, and on cooling this solution crystals separated melting at  $128\text{--}130^{\circ}$ ; after a second crystallisation from hot, concentrated hydrochloric acid, the substance melted at  $129^{\circ}$ .

*The Acid melting at  $209^{\circ}$  (Trans-dimethylsuccinic acid).*

This acid was analysed, with the following results, which agree well with the empirical formula  $\text{C}_6\text{H}_{10}\text{O}_4$ .

	Found.		Calculated.
	I.	II.	
Carbon.....	49.21	49.49	49.32
Hydrogen....	7.12	6.73	6.85

*Trans-dimethylsuccinic acid* is only very sparingly soluble in cold, but readily in boiling water. It is almost insoluble in benzene or chloroform, either hot or cold, but is fairly soluble in alcohol or ether.

*Salts of the Acid.*—To a neutral solution of the ammonium salt was added

- (a.) *Ferric chloride.* A reddish-brown precipitate of the ferric salt was immediately thrown down.
- (b.) *Copper sulphate.* A greenish-blue and very gelatinous precipitate was formed.
- (c.) *Lead nitrate.* A heavy, crystalline precipitate of the lead salt was produced; this was fairly soluble in hot water, and crystallised out again on cooling.
- (d.) *Silver nitrate.* A white precipitate of the silver salt was formed, fairly soluble in cold water.
- (e.) *Calcium chloride.* When calcium chloride was added to a dilute solution of the ammonium salt, no precipitate was produced either in the cold, or even on boiling for a considerable time. When, however, a fairly strong solution of the ammonium salt was used, the calcium salt was immediately precipitated, even in the cold.

We may here remark that the lead, silver, and calcium salts of the *trans*-acid, and especially the last-named, are decidedly more soluble than the corresponding salts of the *cis*-acid.

*The Acid melting at 129° (Cis-dimethylsuccinic acid).*

This acid was analysed, with the following results.

	Found.	Calculated for $C_6H_{10}O_4$ .
Carbon.....	49.38	49.32
Hydrogen :.....	6.88	6.85

*Cis-dimethylsuccinic acid* is fairly soluble in cold and readily in warm water, alcohol, or ether, separating rapidly from its aqueous solution when this is saturated with gaseous hydrogen chloride. It is more soluble in warm benzene and chloroform than the isomeric *trans*-acid.

Its salts are very similar to those of the *trans*-acid, but the calcium, lead, and silver salts are much less soluble in water than the corresponding salts of the *trans*-acid.



*Separation of the Dimethylsuccinic Acids by means of their Calcium Salts.*

The marked difference in the solubilities of the calcium salts of the *cis*- and *trans*-dimethylsuccinic acids affords a very convenient method of separating them, and of obtaining them readily in a state of purity. The method employed by the authors may be briefly described as follows.

Calcium chloride was added to a cold dilute solution of the ammonium salts of the two acids, when, after a short time, a white precipitate of the calcium salt of the *cis*-acid was formed; the whole was then gently warmed, and the precipitate collected with the aid of the pump, washed with a little hot water, and dissolved in hot concentrated hydrochloric acid. On cooling, crystals of the *cis*-acid, melting sharply at  $129^{\circ}$ , were deposited. The filtrate from the first crude precipitate was then concentrated on the water bath, and the small precipitate which separated during the operation, consisting of a mixture of the calcium salts, removed by filtration. On proceeding further with the concentration, a very bulky precipitate came down; this was separated from the mother-liquor with the aid of the pump and after washing with cold water, was dissolved in hot concentrated hydrochloric acid. On cooling, colourless crystals of the *trans*-acid melting at  $204\text{--}209^{\circ}$  were deposited; after recrystallisation from water they melted at  $209^{\circ}$ .

*B.—Preparation of the Symmetrical Dimethylsuccinic acids from Ethylic Methylmalonate and Ethylic  $\alpha$ -Bromopropionate.*

Forty-four grams of ethylic methylmalonate were mixed with a cold solution of 6 grams of sodium in 75 grams of absolute alcohol contained in a flask, and 45 grams of ethylic  $\alpha$ -bromopropionate were carefully added. The mixture at once became hot, and sodium bromide began to separate. On heating the mixture in a water bath in a reflux apparatus for two hours, it became quite neutral; and on pouring the contents of the flask into water, a heavy oil separated. This was extracted with ether, the ethereal solution washed with dilute sodium carbonate solution and with water, dried over calcium chloride, the ether distilled off, and the dark-yellow, oily residue (60 grams) hydrolysed without further purification.

*Hydrolysis of the Oil.*—The oil was slowly added to about twice its weight of potassium hydroxide dissolved in alcohol, and contained in a large flask; there was a considerable development of heat, so that it was necessary to cool the flask well to prevent loss by frothing; the whole was then heated for six hours in a reflux apparatus on the water bath. A potassium salt soon separated, and after the conclusion of the hydrolysis, water was added to the liquid until this had dissolved,

the solution was poured into an evaporating basin, and concentrated on a water bath until all the alcohol had been driven off. The alkaline liquid was then cooled, carefully acidified with dilute hydrochloric acid, and repeatedly extracted with pure ether; the ethereal solution was dried over calcium chloride, the ether driven off, and the oil which was left heated in an oil bath at  $200^{\circ}$  until the evolution of carbonic anhydride entirely ceased. The oily residue was then dissolved in hot water, the solution boiled with animal charcoal, and filtered whilst hot; on cooling, the filtrate deposited a mass of white crystals, which were separated from the mother liquor by filtration, and washed well with cold water. On recrystallising these from hot concentrated hydrochloric acid, they melted at  $209^{\circ}$ ; a second recrystallisation from concentrated hydrochloric acid did not alter the melting point. This acid on analysis yielded the following results.

	Found.		Calculated for $C_6H_{10}O_4$ .
	I.	II.	
Carbon.....	49.23	49.55	49.32
Hydrogen.....	6.75	6.92	6.85

and was identical in all its properties with the *trans*-acid melting at the same temperature obtained from ethylic  $\alpha\alpha$ -dimethylecyanosuccinate as described in the preceding section.

The filtrate, after removal of the acid melting at  $209^{\circ}$  was concentrated somewhat, and then repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off; a small quantity of a viscous oil was left, which, on standing, solidified almost entirely. This solid mass was ground up and washed with cold benzene to remove any oily matter, and the residue recrystallised from hot concentrated hydrochloric acid; in this way an acid was obtained melting at  $125$ – $127^{\circ}$ , which, after a second recrystallisation, melted at  $129^{\circ}$ , and was identical in all its properties with the *cis*-acid melting at  $130^{\circ}$  obtained from ethylic  $\alpha\alpha$ -dimethylecyanosuccinate. This acid on analysis yielded the following results.

	Found.	Calculated.
Carbon .....	49.30	49.32
Hydrogen .....	6.67	6.85

The amount of *cis*-dimethylsuccinic acid obtained by the method above described is comparatively small, not more than about one-fourth of the weight of the *trans*-acid formed at the same time.

*Behaviour of the Dimethylsuccinic Acids on Prolonged Heating with Concentrated Hydrochloric acid in Sealed Tubes at  $180^{\circ}$ .*

1. About 5 grams of the *trans*-dimethylsuccinic acid (m. p.  $209^{\circ}$ ) were sealed up in a tube with about 40 c.c. of concentrated hydro-

chloric acid, and heated at  $180^{\circ}$  for eight hours. On cooling, the crystals, which had separated were collected, well washed with water, and dried at  $100^{\circ}$ ; they melted at  $200\text{--}204^{\circ}$ , and, after recrystallisation from water, at  $208^{\circ}$ . The mother liquor was extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled off, when a very small quantity of an oily substance was left; this partially solidified on long standing, and the solid, after drying on a porous plate, was found to melt at  $117\text{--}124^{\circ}$ . It probably consisted of the *cis*-acid (m. p.  $129^{\circ}$ ), but the amount was exceedingly small, nearly the whole of the *trans*-acid being recovered unchanged.

2. The *cis*-dimethylsuccinic acid (m. p.  $129^{\circ}$ ) was heated in a tube with concentrated hydrochloric acid under pressure, as described in the previous experiment; the crystals which separated on cooling were collected, washed with water, and dried at  $100^{\circ}$ . They consisted of crude *trans*-dimethylsuccinic acid and melted between  $190^{\circ}$  and  $200^{\circ}$ , and, after recrystallisation from water, at  $201\text{--}205^{\circ}$ . The mother liquor was extracted with pure ether, and, as in the case of the previous experiment, a very small amount of the unchanged *cis*-acid was obtained.

Thus it is evident that, on heating the *trans*-acid under pressure with concentrated hydrochloric acid at  $180^{\circ}$ , it is only partially transformed into the *cis*-acid, the greater part of it being unchanged, and that when the *cis*-acid is subjected to the same treatment, it is for the most part converted into the *trans*-modification.

## PART II.—THE ANHYDRIDES OF *Cis*- AND *Trans*-DIMETHYLSUCCINIC ACIDS.

### A. Behaviour of the Dimethylsuccinic Acids on Prolonged Heating at $210\text{--}215^{\circ}$ .

1. One gram of the *trans*-acid (m. p.  $209^{\circ}$ ) was heated in a test-tube immersed in an oil bath, the temperature of which was raised fairly rapidly to about  $170^{\circ}$ , and afterwards gradually to  $210^{\circ}$ . At about  $205^{\circ}$ , the substance began to sublime without melting, and condensed on the upper and cooler portion of the tube in beautiful, asymmetric needles, which, after being spread on a porous plate, melted at  $195\text{--}198^{\circ}$ . When the temperature of the bath had risen to  $210\text{--}211^{\circ}$ , the substance melted, and water was given off; the bath was now kept at  $210\text{--}215^{\circ}$  for half an hour, when the evolution of steam seemed to have ceased entirely. As the contents of the test-tube solidified on cooling, it was broken, and the solid mass spread on a porous plate; it was found to melt roughly between  $65^{\circ}$  and  $85^{\circ}$ . When treated in the cold with a dilute solution of sodium carbonate,



no effervescence could be detected, showing, therefore, that the acid had been completely converted into an anhydride. It was then dissolved in pure ether, and the ether allowed to gradually evaporate, when beautiful, colourless crystals were deposited melting at  $84-86^{\circ}$ , and identical with the anhydride prepared from the *cis*-acid by treatment with acetyl chloride. It dissolved readily in hot water, and after the solution had been cooled and saturated with gaseous hydrogen chloride, the *cis*-acid separated in crystals melting at  $126-128^{\circ}$ .

2. One gram of the *cis*-acid was subjected to the same treatment as has been described in the previous experiment; at a temperature rather above  $200^{\circ}$ , water was readily given off; the crude product solidified on cooling, and then melted between  $70^{\circ}$  and  $80^{\circ}$ . When treated with a cold, dilute solution of sodium carbonate, there was no evolution of carbonic anhydride, indicating that the transformation into anhydride was complete. The solid mass, which, after recrystallisation from absolute ether melted at  $87^{\circ}$ , was dissolved in hot water, the solution cooled, and saturated with gaseous hydrogen chloride, when the *cis*-acid separated in crystals melting at  $128-129^{\circ}$ .

Both the dimethylsuccinic acids, therefore, when heated at  $210-215^{\circ}$ , are converted into the *same* anhydride, which must be the anhydride of the *cis*-acid, as it yields this acid when treated with water.

*B. Behaviour of the Dimethylsuccinic acids on Distillation at the Ordinary Atmospheric Pressure.*

1. Two grams of the *trans*-acid were distilled in a small flask into which a thermometer was inserted; a heavy liquid came over between  $230^{\circ}$  and  $235^{\circ}$ , which solidified on cooling. The solid mass melted gradually between  $70^{\circ}$  and  $82^{\circ}$ , and when treated in the cold with a dilute solution of sodium carbonate, a small portion dissolved with effervescence, and from this solution a small quantity of an acid melting at about  $195^{\circ}$  was obtained. The anhydride, after treatment with sodium carbonate, and drying on a porous plate, melted at  $83-86^{\circ}$ , which was raised to  $88^{\circ}$  by recrystallisation from absolute ether. This anhydride, with water, yielded the *cis*-acid melting at  $127-129^{\circ}$ .

2. On distilling the *cis*-acid in the manner described in the previous experiment, a liquid passed over between  $230^{\circ}$  and  $235^{\circ}$ , which completely solidified on standing. The solid mass, which melted between  $78^{\circ}$  and  $85^{\circ}$ , showed no signs of effervescence when treated in the cold with a dilute solution of sodium carbonate, and, after recrystallisation from absolute ether, melted at  $88^{\circ}$ . When heated with water, it yielded the original *cis*-acid again.



Thus, on distillation under ordinary pressure, both acids are converted into the *cis*-anhydride; in the case of the *trans*-acid, however, the conversion is incomplete, a portion of the acid distilling over apparently unchanged.

C. *Distillation of the Trans-acid under Reduced Pressure.*

This experiment was undertaken with a view of ascertaining whether the *trans*-acid on distillation under reduced pressure would yield the same anhydride as it did when distilled under ordinary pressure; it was found, however, that it sublimed very readily under reduced pressure, and apparently for the most part unchanged. The sublimate dissolved very readily in dilute sodium carbonate with effervescence, but it had no constant melting point; a small portion melted at a temperature as low as  $40^{\circ}$ , but by far the greater part of it showed no signs of melting until the temperature had risen to  $190^{\circ}$ , when it gradually melted between  $190^{\circ}$  and  $198^{\circ}$ . It seems probable, therefore, that when the acid is sublimed under these conditions it is to a small extent converted into an anhydride, although we were unable to isolate a pure anhydride from the sublimate.

D. *Behaviour of the Acids on heating with Acetyl Chloride or Acetic Anhydride.*

1. About 5 grams of the *trans*-acid were mixed with about 7 c.c. of acetyl chloride, and the whole gently heated in a small reflux apparatus for 10 minutes, until the whole of the acid had just dissolved; it was then placed in a vacuum over solid potash, when the excess of acetyl chloride rapidly volatilised, leaving a yellowish-white crystalline mass, which was then dried on a porous plate in a vacuum. The crude product had no constant melting point, part melted between  $30^{\circ}$  and  $40^{\circ}$ , but quite half of it did not melt until the temperature had risen to  $160^{\circ}$ , indicating that a considerable portion of the original acid had remained unchanged. It was accordingly mixed with more acetyl chloride, and heated gently in a reflux apparatus on a sand bath for half an hour; the product, isolated as described above, now melted sharply at  $43^{\circ}$ . The substance was then heated for about 20 minutes in a reflux apparatus on a sand bath with acetic anhydride, the excess of acetic anhydride distilled off under reduced pressure, and the liquid residue placed in a vacuum over solid potash, where, after standing several days, it solidified to a pure white mass; this was spread out on a porous plate and left in a vacuum over solid potash, after which it melted very sharply at  $43^{\circ}$ .

The substance was analysed with the following results.

	Found.	Calculated for $C_6H_8O_3$ .
Carbon .....	55.82	56.25
Hydrogen .....	6.48	6.25

On dissolving this anhydride in hot water, and cooling the solution, white crystals separated, which, after drying on a porous plate, melted at  $208^\circ$ , and were in all respects identical with *trans*-dimethylsuccinic acid. The substance melting at  $43^\circ$  is, therefore, the anhydride of *trans*-dimethylsuccinic acid.

2. Five grams of the *trans*-acid were mixed with 15 grams of acetic anhydride, the whole heated on the sand bath for three hours in a reflux apparatus, and then fractionally distilled under a pressure of 30 mm.; after the greater part of the acetic anhydride had come over, the temperature rose rapidly to  $160^\circ$ , when the receiver was changed, and the portion distilling over between  $160^\circ$  and  $180^\circ$  collected separately, and placed in a vacuum over solid potash. After the substance had become solid, the crystals were dried on a porous plate in a vacuum, when they melted between  $40^\circ$  and  $50^\circ$ , mostly, however, in the neighbourhood of  $43^\circ$ . A portion of the substance was treated in the cold with a dilute solution of sodium carbonate, but not the slightest effervescence could be detected, showing that no free acid was present. This anhydride was again heated with acetic anhydride for three hours, and the treatment described above repeated. Finally we obtained the *cis*-anhydride melting at  $88^\circ$ , which with water yielded the *cis*-acid melting at  $129^\circ$ .

From this experiment, it seemed probable that the *trans*-acid, when heated with acetic anhydride, yields first of all its own anhydride (m. p. =  $43^\circ$ ), but that on prolonged heating with acetic anhydride this is converted into the *cis*-anhydride melting at  $88^\circ$ . This conclusion was confirmed as follows: A small portion of the *trans*-anhydride melting at  $43^\circ$ , obtained in D 1, was heated for several hours with acetic anhydride in a reflux apparatus, the excess of acetic anhydride distilled off under reduced pressure, and the residual liquid placed in a vacuum over solid potash. After several days, the liquid deposited crystals, which when dried in a vacuum on a porous plate, were found to melt at  $87$ – $88^\circ$ , and with water yielded the *cis*-acid.

Thus the *trans*-anhydride, on prolonged heating with acetic anhydride, is converted into the *cis*-anhydride.

3. Five grams of the *cis*-acid were heated with acetic anhydride for three hours on a sand bath in a reflux apparatus, the excess of acetic anhydride distilled off under reduced pressure, and the residual liquid placed in a vacuum over solid potash. On long standing, the liquid crystallised, and the crystals, after drying on a porous plate, melted at  $87^\circ$ , and on being dissolved in hot water yielded the *cis*-acid melting at  $128$ – $129^\circ$ .

The *cis*-anhydride (m. p.  $88^{\circ}$ ) was analysed with the following results.

	Found.	Calculated for $C_6H_8O_3$ .
Carbon .....	55.99	56.25
Hydrogen .....	6.60	6.25

4. The *cis*-acid was dissolved in a slight excess of acetyl chloride, the solution gently warmed on the sand bath in a reflux apparatus for 20 minutes, and placed over solid potash in a desiccator, which was then exhausted; the acetyl chloride was thus rapidly volatilised, and the residue crystallised on standing. The crystals, after drying in a vacuum on a porous plate, were found to consist of the *cis*-anhydride melting at  $88^{\circ}$ .

*Owens College, Manchester.*

TRIMETHYLSUCCINIC AND  $\alpha\alpha_1$ -DIMETHYL-  
GLUTARIC ACIDS.

BY

W. A. BONE, M.Sc., Ph.D.,

AND

W. H. PERKIN, JUN., F.R.S.

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[From the Transactions of the Chemical Society, 1895.]





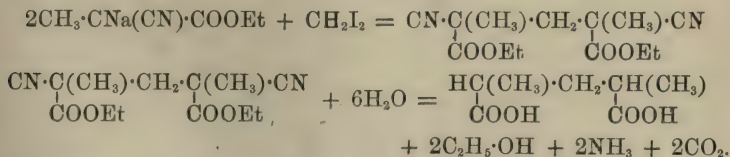
## Trimethylsuccinic and $\alpha\alpha_1$ -Dimethylglutaric acids.

By WM. A. BONE, M.Sc., Ph.D. (late Fellow of Victoria University),  
and W. H. PERKIN, jun., F.R.S.

### *Introduction.*

DURING the last few years, there has been considerable discussion as to the conditions of formation and properties of the isomeric acids which form the subject matter of this communication, and in spite of a great deal of experimental work it is only quite recently that the various issues raised in the controversy have been at all clearly understood.

In 1889, Zelinsky (*Ber.*, 1889, **22**, 2823) first obtained a mixture of two isomeric  $\alpha\alpha_1$ -dimethylglutaric acids by acting on the sodium compound of ethylic  $\alpha$ -cyanopropionate with methylenic iodide, and then hydrolysing the product and heating the acids thus obtained to 200°. The reactions involved in this process may be thus written.

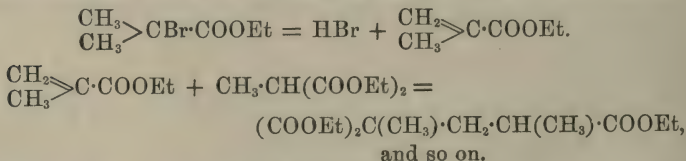


He separated the two isomeric acids by fractional crystallisation from a mixture of benzene and light petroleum. The more insoluble acid melted at 128° and the more soluble at 102° to 104°, but they resembled each other very closely in their other properties.

In the following year, Bischoff and Mintz (*Ber.*, 1890, **23**, 647) described as trimethylsuccinic acid an acid melting at 105°, and yielding an anhydride melting between 67° and 82°, which they had pre-

pared from the product of the action of ethylic  $\alpha$ -bromisobutyrate on an alcoholic solution of the sodium compound of ethylic methylmalonate. Shortly afterwards, Bischoff (*Ber.*, 1890, **23**, 1464) repeated Zelinsky's preparation of the  $\alpha\alpha_1$ -dimethylglutaric acids, and obtained an acid melting at 100–101°. He found its dissociation constant to be identical with that of the "trimethylsuccinic acid" prepared by himself and Mintz, namely  $K = 0.0054$ . Despite this fact, he considered that the latter was a true trimethylsuccinic acid, mainly on account of its method of formation, as it was difficult to see how any acid other than trimethylsuccinic could be formed in this way. Auwers and Jackson (*Ber.*, 1890, **23**, 1599) argued from the smallness of its dissociation constant that Bischoff was mistaken in calling his acid "trimethylsuccinic acid," and that it was in reality a dimethylglutaric acid. Ostwald had shown that in the substituted succinic acids the dissociation constant increases in value with the number of alkyl groups, whereas the dissociation constant of Bischoff's acid is actually below that of succinic acid itself ( $K = 0.00665$ ). Further, the identity of its dissociation constant and that of Zelinsky's  $\alpha\alpha_1$ -dimethylglutaric acid, and the fact that when treated with bromine according to the Hell-Vollard-Zelinsky method it yielded the anhydride of a dibromo-acid, and therefore contained two  $\alpha$ -hydrogen atoms, showed that in reality it was a dimethylglutaric acid. To explain its formation by the action of ethylic  $\alpha$ -bromisobutyrate on the sodium compound of ethylic methylmalonate, Auwers supposed that under the conditions of the experiment the ethylic  $\alpha$ -bromisobutyrate loses hydrogen bromide and yields ethylic methacrylate, this then condenses with the sodium compound of ethylic methylmalonate forming the ethylic salt of a tricarboxylic acid, which on subsequent hydrolysis and heating of the resulting acid to 200° would give  $\alpha\alpha_1$ -dimethylglutaric acid.\*

The reactions which are supposed to occur may be thus expressed.

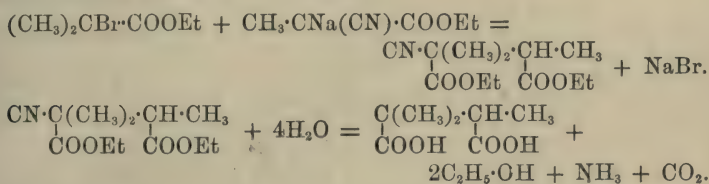


Bischoff (*Ber.*, 1891, **24**, 1041) then admitted the correctness of Auwer's explanation, but on further investigation he showed that if ethylic  $\alpha$ -bromisobutyrate and the sodium compound of ethylic methyl-

\* We may here note that a very similar explanation was given by Hell of the fact that when ethylic  $\alpha$ -bromisobutyrate is treated with molecular silver, and the product hydrolysed, a mixture of tetramethylsuccinic and trimethylglutaric acids is obtained (*Ber.*, 1890, **23**, 298).

malonate were allowed to interact in xylene at  $180^\circ$ , instead of in alcoholic solution, a mixture of ethereal salts was obtained which on hydrolysis yielded, besides the dimethylglutaric acid melting at  $102^\circ$  to  $105^\circ$ , a large quantity of an isomeric acid melting at  $139.5^\circ$ , and having a dissociation constant  $K = 0.0310$ , and which he therefore concluded was trimethylsuccinic acid.

Zelinsky (*Ber.*, 1891, **24**, 459) next prepared trimethylsuccinic acid by the action of ethylic  $\alpha$ -bromisobutyrate on the sodium compound of ethylic cyanopropionate in alcoholic solution, subsequently hydrolysing the ethylic cyanotrimethylsuccinate thus formed with dilute sulphuric acid, and then heating the product at  $200^\circ$  until carbon dioxide ceased to be evolved.



The product, however, was in reality a mixture; and by fractional crystallisation from a mixture of benzene and light petroleum he isolated two acids; the less soluble melting at  $140$ – $141^\circ$  and having a dissociation constant  $K = 0.0322$ ; the more soluble melting at  $100$ – $101^\circ$  and having a dissociation constant  $K = 0.0063$ . He maintained that they were *both* trimethylsuccinic acids, and that the acid of lower melting point was quite distinct from the dimethylglutaric acid melting at about the same temperature.

Auwers (Auwers and Köbner, *Ber.*, 1891, **24**, 1923) strongly dissented from Zelinsky's view of the nature of his acid of lower melting point, and showed that its chemical and physical properties so closely resembled those of the dimethylglutaric acid melting at  $105^\circ$  that the two substances must be identical. Both acids when treated with acetyl chloride yielded the same anhydride melting at  $95^\circ$ , and this on treatment with water gave an acid melting at  $128^\circ$ , identical with the dimethylglutaric acid of higher melting point. Zelinsky, however, was unconvinced, and still remains so. Of course the formation of dimethylglutaric acid from ethylic cyanopropionate and ethylic bromisobutyrate is readily understood if it be assumed that the reaction takes place in a similar way to that by which Bischoff obtained dimethylglutaric acid from ethylic methylmalonate and ethylic  $\alpha$ -bromisobutyrate (see p. 417).

In 1893, Koenigs (*Ber.*, 1893, **26**, 2337), by the oxidation of camphoric acid with chromic acid, obtained a trimethylsuccinic acid, which melted at  $139$ – $140^\circ$ , and was in all respects identical with Bischoff's



synthetical trimethylsuccinic acid. In the same year, Helle (*Inaug. Diss.*, Bonn, 1893), by the dry distillation of camphoronic acid, obtained a trimethylsuccinic acid melting at  $131^{\circ}$ , which, with acetyl chloride, yielded an anhydride melting at  $31^{\circ}$ ; this acid he also considered was identical with the trimethylsuccinic acid prepared synthetically by Bischoff.

Early last year, the authors were desirous of preparing trimethylsuccinic acid in considerable quantity, and on studying the literature of the subject with the view of finding the best method of preparation, they found such a confused mass of experimental data, that it was very difficult to form any opinion in the matter, as the following acids had all been described as "trimethylsuccinic acid."

	Melting point.	K.	Authority.
(1.)	{ $140-141^{\circ}$ $139-140$	0.0322 0.0310	Zelinsky. Bischoff, Koenigs.
(2.)	131	—	Helle.
(3.)	100—101	0.0063	Zelinsky.

Now, although Helle considered his acid to be identical with that prepared by Bischoff and Koenigs, the difference in the melting points tended to throw some doubt on his view, especially as he had obtained his acid so pure as to be able to subject it to a *detailed* crystallographic study. Even supposing the two acids were really identical, there still remained Zelinsky's acid of lower melting point to be accounted for. Trimethylsuccinic acid contains one asymmetric carbon atom, and therefore, according to the van't Hoff-Le Bel theory, it should only exist in *one* inactive form. If there are, as Zelinsky contends, *two* inactive modifications, then the theory in question is inadequate to explain the facts; the case being a crucial one, the authors decided to subject it to a careful re-investigation, some of the results of which are detailed in this paper.

Quite recently, February 1895, Auwers (*Ber.*, **28**, 623) published a preliminary notice of some further work on the subject. On preparing trimethylsuccinic acid by every known method, he finds that it exists in *one* form only, melting at  $147^{\circ}$ , and yielding an anhydride which melts at  $31^{\circ}$ . He also brings further evidence against the view that Zelinsky's acid of lower melting point is a trimethylsuccinic acid, and finds that it is really a mixture of two  $\alpha\alpha$ -dimethylglutaric acids in molecular proportion, the one melting at  $126^{\circ}$  (*cis*), and the other at  $140-141^{\circ}$  (*trans*). The results of our experiments may be summarised as follows.

We have prepared trimethylsuccinic acid in quantity by two quite different methods, namely, the action of ethylic  $\alpha$ -cyanopropionate on ethylic  $\alpha$ -bromisobutyrate (Zelinsky's method), and by the action of

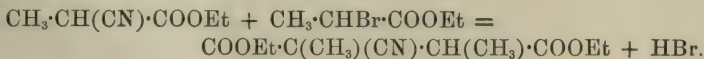
ethylic  $\alpha$ -bromisobutyrate on ethylic sodiomethylmalonate at  $180^\circ$  in xylene solution (Bischoff's method), and find that it undoubtedly only exists in *one* form, which melts at  $152^\circ$  (Auwers gives  $147\text{--}148^\circ$ ), and yields an anhydride melting at  $38.5^\circ$  (Auwers gives  $31^\circ$ ). Thus we are able to confirm Auwers' views as to the nature of this acid; with regard to the isomeric  $\alpha\alpha_1$ -dimethylglutaric acids, the authors have isolated two, one melting at  $128^\circ$  (cis-), and the other at  $105^\circ$  to  $107^\circ$ . Both these acids, on heating with acetic anhydride, yield the *same* anhydride, melting at  $93^\circ$  to  $94^\circ$ , which, with water, yields the cis-acid, melting at  $128^\circ$  again. The authors are engaged in an examination of the  $105^\circ$  acid, which is not yet complete enough for publication; up to the present, however, their results are not in agreement with those of Auwers.

During the course of their experiments, the authors have isolated ethylic  $\alpha\beta$ -dicyanopropionate,  $\text{CH}_2(\text{CN})\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$ , a substance which crystallises in needles melting at  $118^\circ$ , and also trimethylcyano-propionic acid,  $\text{CH}_3\cdot\text{CH}(\text{CN})\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOH}$ , an interesting acid which crystallises in colourless needles melting at  $126^\circ$ , and, on treatment with acetic anhydride, yields a beautifully crystalline acetyl derivative,  $\text{CH}_3\cdot\text{C}(\text{CO}\cdot\text{CH}_3)(\text{CN})\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOH}$ , melting at  $67^\circ$ . The authors are engaged in further work on these acids, the results of which they reserve for a future communication.

## EXPERIMENTAL PART.

### *Preparation of Ethylic $\alpha$ -Cyanopropionate, $\text{CH}_3\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$ .*

The ethylic  $\alpha$ -cyanopropionate required for this investigation was prepared by the action of potassium cyanide on an alcoholic solution of ethylic  $\alpha$ -bromopropionate. This reaction was first employed by Zelinsky (*Ber.*, 1888, **21**, 3162), who allowed the substances in question to interact on a water bath at the ordinary pressure. The yield of ethylic  $\alpha$ -cyanopropionate was very unsatisfactory, as the product of the action contained not only a considerable quantity of unchanged ethylic  $\alpha$ -bromopropionate, but also a large amount of ethylic dimethylcyanosuccinate, the latter being formed by the condensation of some of the ethylic  $\alpha$ -cyanopropionate with the unchanged ethylic  $\alpha$ -bromopropionate, as follows.



Thus, from 258 grams of ethylic  $\alpha$ -bromopropionate, he obtained 45 grams of unchanged substance, only 27 grams of ethylic  $\alpha$ -cyanopropionate, and no less than 64 grams of ethylic dimethylcyanosuccinate.

The authors set to work to see whether by modifying the conditions of the experiment they could not improve the yield of ethylic  $\alpha$ -cyanopropionate, and ultimately found that by working under pressure a much better result could be obtained. The method they finally adopted is as follows.

Fifty grams of finely-powdered potassium cyanide are added to a mixture of 100 grams of ethylic  $\alpha$ -bromopropionate and 50 grams of absolute alcohol contained in a dry soda-water bottle; the bottle is then tightly corked and heated for six to eight hours at  $100^{\circ}$  in a water bath. It is found convenient to heat five or six such bottles at one time. The contents of the bottles, which are yellowish-brown (and in some cases dark brown), and smell strongly of hydrogen cyanide, are now filtered at the pump, and the residual potassium cyanide and bromide washed with a little alcohol. As much of the alcohol as possible is distilled off from the filtrate on the water bath, and the residue poured into water, when a reddish-brown oil separates; this is extracted with ether, the ethereal solution, after being well washed with water and dilute sodium carbonate solution, is dried over calcium chloride, and the ether distilled off. The residual reddish oil consists principally of three substances, namely, ethylic  $\alpha$ -bromopropionate, ethylic  $\alpha$ -cyanopropionate, and ethylic dimethylcyanosuccinate; these may be separated by careful fractionation, which is best effected under reduced pressure, using a fractionating column and a water condenser. Under a pressure of 30–40 mm., the unchanged ethylic  $\alpha$ -bromopropionate distils for the most part between  $77^{\circ}$  and  $85^{\circ}$ , and then, if the fractionation has been carefully conducted, the thermometer rises somewhat rapidly to  $103^{\circ}$ , between which temperature and  $110^{\circ}$  ethylic  $\alpha$ -cyanopropionate passes over as a colourless oil. It is well to interrupt the process at this juncture, and to continue the fractionation in an ordinary distilling flask without a column. The thermometer now rises very rapidly, and at a temperature of  $195$ – $200^{\circ}$ , under 80 mm., ethylic dimethylcyanosuccinate passes over as a pale yellow oil; if this be very rapidly cooled, a small quantity of a beautifully crystalline solid separates out on the sides of the condenser, the investigation of which is described in the succeeding paragraph. The following table gives the quantities of the three principal products obtained by the modified process (from 100 grams of ethylic  $\alpha$ -bromopropionate used) as compared with those got on employing the earlier method of Zelinsky.

	New.	Old.
Unchanged ethylic $\alpha$ -bromopropionate. . . . .	28	33
Ethylic $\alpha$ -cyanopropionate. . . . .	20	12
Ethylic $\alpha\alpha$ -dimethylcyanosuccinate. . . . .	10	7



*Ethyl Dicyanopropionate*,  $\text{CH}_2(\text{CN})\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$ .

This substance is only formed in very small quantities in the foregoing experiment, the products of eight or ten bottles yielding only some 2 or 3 grams; it is deposited on the sides of the condenser in light, white flakes, during the distillation of the ethylic dimethylcyanosuccinate. It seems to be rather soluble in ethylic dimethylcyanosuccinate, and the more rapidly the vapour of the latter is condensed, the more of this solid body is obtained; it is fairly soluble in benzene, and, although almost insoluble in cold light petroleum, it may be crystallised from the hot solvent in beautiful, silky, pale yellow needles, which melt at  $118^\circ$ . On analysis, it yielded numbers closely agreeing with the empirical formula  $\text{C}_7\text{H}_8\text{O}_2\text{N}_2$ .

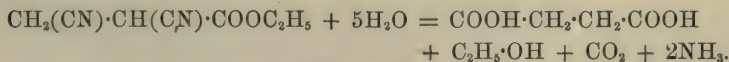
	Carbon.	Hydrogen.	Nitrogen.
Found . . . . .	55.00	5.99	18.45 per cent.
Calculated . . .	55.26	5.26	18.42 ,,

A determination of the molecular weight by Raoult's method gave the following results.

0.123 gram substance dissolved in 19.00 grams of benzene produced a depression of  $0.215^\circ$  in the freezing point.

$$\therefore \text{Molecular weight} = 147.5. \quad \text{C}_7\text{H}_8\text{O}_2\text{N}_2 = 152.$$

We concluded that the substance was ethylic  $\alpha\beta$ -dicyanopropionate,  $\text{CH}_2(\text{CN})\cdot\text{CH}(\text{CN})\cdot\text{COOC}_2\text{H}_5$ , and in confirmation of this view we found that, when boiled with concentrated hydrochloric acid for some time, it yielded ammonium chloride and an acid which gave the qualitative reactions of succinic acid, which should be formed according to the equation



The formation of this substance probably takes place as follows. During the bromination of the propionic acid, a small quantity of the bromopropionic acid loses hydrogen bromide with formation of acrylic acid, according to the equation  $\text{CH}_3\cdot\text{CHBr}\cdot\text{COOH} = \text{HBr} + \text{CH}_2\cdot\text{CH}\cdot\text{COOH}$ . This then combines with the excess of bromine to form  $\alpha\beta$ -dibromopropionic acid,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{COOH}$ , the ethereal salt of which, when heated with potassium cyanide, yields the corresponding dicyano-compound. Other cases, somewhat similar to this, have been noticed in these laboratories.

*Preparation of Ethylic Trimethylcyanosuccinate,*  
 $\text{COOEt}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}(\text{CH}_3)(\text{CN})\cdot\text{COOEt}$ .

The method employed for the preparation of this substance was



essentially that proposed by Zelinsky (*Ber.*, 1891, **24**, 468), and may be briefly described as follows.

127 grams of ethylic  $\alpha$ -cyanopropionate are mixed with a cold solution of 23 grams of sodium in 280 grams of absolute alcohol, and 205 grams of ethylic  $\alpha$ -bromisobutyrate carefully added. There appears to be little or no action in the cold, but, on heating the mixture on the water bath in a reflux apparatus, sodium bromide soon separates, and, after some two hours, the solution becomes quite neutral. The contents of the flask are then poured into a large volume of water, when the ethylic trimethylcyanosuccinate separates as a dark yellow oil, which is extracted with ether. The ethereal solution is washed with water and dilute sodium carbonate solution, and dried over calcium chloride; the ether is then distilled off and the residual oil carefully fractionated under diminished pressure, when ethylic trimethylcyanosuccinate is obtained, boiling at 193—195° under a pressure of 40 mm. The yield is nearly theoretical.

#### *Hydrolysis of the Ethereal Salt.*

Zelinsky (*loc. cit.*) hydrolysed this ethereal salt by boiling it with dilute sulphuric acid; the authors, however, found this method very unsuitable, as, after heating for several days, a considerable amount of oil still remained unchanged. They decided therefore to employ alcoholic potash as the hydrolysing agent, and conducted the operation as follows.

The ethereal salt is slowly added to double its weight of potassium hydroxide dissolved in alcohol, and contained in a large flask; the addition is accompanied by a very considerable development of heat, and the flask, therefore, must be well cooled to prevent loss by frothing. A potassium salt separates almost immediately, and the contents of the flask become quite pasty, necessitating the addition of more alcohol. After all the ethereal salt has been added, the flask is connected with a reflux condenser and heated for 8—10 hours in a water bath, when a large amount of ammonia is evolved. The contents of the flask are then diluted with water until the potassium salt all dissolves, the solution poured into a large evaporating basin, and boiled vigorously for two or three days, fresh water and potassium hydroxide being added at intervals. To *completely* hydrolyse the ether is a matter of considerable difficulty, and we shall show that, after *continued* heating with potassium hydroxide in the manner just described until the evolution of ammonia nearly ceases, a very fair quantity of the potassium salt of trimethylcyanopropionic acid is left undecomposed. The alkaline liquid is concentrated to a small volume on the water bath, cooled, and carefully acidified with hydrochloric acid; it is then repeatedly extracted with pure ether, the

etheral solution dried over calcium chloride, the ether distilled off, and the residual oil heated in an oil bath at  $200^\circ$  until the evolution of carbonic anhydride entirely ceases.

In order to obtain the acids as pure as possible, it is advisable to distil the crude product under reduced pressure. Under a pressure of 100 mm. the greater part passes over between  $190^\circ$  and  $260^\circ$  as a colourless, pungent oil, consisting of a mixture of the acids and their anhydrides.

*Separation of the Acids.*—The anhydrides are converted into acids by dissolving them in hot water and evaporating the solution to dryness on the water bath; on cooling, a solid mass, consisting of the mixed acids, is left behind, which melts gradually between  $70^\circ$  and  $95^\circ$ . Zelinsky endeavoured to effect their separation by fractional crystallisation from a mixture of benzene and light petroleum, as stated in the introduction to this paper. The authors tried this method, but found that, although it was possible to effect a partial separation in this way, none of the fractions had a very definite melting point; fractional crystallisation from concentrated hydrochloric acid was then tried, but this gave still less satisfactory results. Finally, however, experiments on the fractional crystallisation of the calcium salts enabled the authors to devise a good method for isolating the pure acids, which is as follows. The mixture of the acids is dissolved in a small quantity of water, dilute ammonia added in slight excess, and, after heating the ammoniacal solution on the water bath for a short time, allowing it to remain overnight; a large crop of long, colourless needles of cyanotrimethylpropionic acid (A) separates, and are removed by filtration. On adding a little more ammonia to the filtrate and again concentrating, more of the needles are deposited on cooling; this operation is repeated until no more needles appear, even after the liquid has stood several hours. The clear liquid is now diluted in a large beaker with a considerable quantity of water, and mixed with an excess of calcium chloride solution. The beaker is now placed on a sand bath and its contents boiled for about half an hour, during which time the insoluble calcium salt (B) of trimethylsuccinic acid gradually separates. The liquid is now filtered while still hot, with the aid of the pump, and the calcium salt remaining behind is rapidly washed with a little hot water. If the filtrate is concentrated somewhat on the water bath, a further quantity of the calcium salt separates.

The mixed acids present in the filtrate as calcium salts are recovered by decomposing them with excess of strong hydrochloric acid, extracting with ether, and evaporating. The hard, crystalline residue, which melts gradually between  $90^\circ$  and  $115^\circ$ , is dissolved in a slight excess of dilute ammonia, and the whole process detailed

above is repeated, when more cyanotrimethylpropionic acid and a further quantity of the insoluble calcium salt of trimethylsuccinic acid are obtained. Finally, the filtrate is again concentrated to a small volume on the water bath, decomposed by boiling with concentrated hydrochloric acid, and allowed to stand for some time, when a large crop of perfectly white crystals separates; these are collected, and, after recrystallisation from concentrated hydrochloric acid and drying on a porous plate, melt sharply at  $127^{\circ}$ . This substance (C) proved to be one of the modifications of  $\alpha\alpha_1$ -dimethylglutaric acid, which is much more insoluble in strong hydrochloric acid than the other isomeride.

The hydrochloric acid filtrate from this acid is again extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off, when a solid acid is left, which melts gradually between  $95^{\circ}$  and  $110^{\circ}$ . On dissolving this in hot benzene, and allowing the solution to slowly evaporate at the temperature of the room, crystals are gradually deposited; when about half the benzene has volatilised, the liquid is poured off, and the acid is recrystallised from a small quantity of hot benzene, and dried on a porous plate. The crystals then melt at  $105^{\circ}$  to  $107^{\circ}$ .

As the benzene mother liquors still contain a considerable quantity of acid, the benzene is distilled off, and the oily residue is left for a week or two, when it becomes semi-solid; by careful treatment with benzene more of the acid, melting at  $105^{\circ}$  to  $107^{\circ}$ , may be obtained, but after as much as possible of this has been recovered an oil remains which is excessively soluble in benzene and water, and does not solidify even on standing in a vacuum several weeks at a low temperature (below the freezing point of water). This oil has not yet been investigated.

In this way, we have isolated from the original mixture of acids the four following compounds.

- A. The colourless needles.
- B. An insoluble calcium salt.
- C. An acid melting at  $127^{\circ}$ .
- D.     ,,             ,,          $105^{\circ}$  to  $107^{\circ}$ .

We shall now discuss these in detail.

A. *Trimethylcyanopropionic acid*,  $\text{COOH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CN}$ .

The colourless needles melted at  $123$ — $125^{\circ}$ , but, after recrystallisation from hot concentrated hydrochloric acid, they melted sharply at  $126^{\circ}$ . They are sparingly soluble in cold water and in hydrochloric acid, but dissolve easily in these solvents on boiling, and separate again on cooling. The acid is fairly soluble in cold benzene, but



insoluble in cold light petroleum, or in a mixture of benzene and light petroleum; it is very readily soluble in chloroform or alcohol.

On analysis the following numbers were obtained, which agree well with the empirical formula  $C_7H_{11}O_2N$ .

	Carbon.	Hydrogen.	Nitrogen.
Found . . . . .	60.01	7.88	10.23, 9.88 per cent.
Calculated. . .	59.58	7.80	9.99 „

This acid is an interesting substance in many respects. If a solution of its ammonium salt is heated on a water bath, the salt decomposes, ammonia is evolved, and, on cooling, the free acid separates. Although the acid contains a cyanogen group, it may be recrystallised from hot concentrated hydrochloric acid without decomposition; in fact, it is only on *prolonged* heating with the ordinary hydrolysing agents that it is decomposed.

The silver salt was prepared by dissolving the acid in dilute ammonia, gently warming the solution to get rid of the slight excess of ammonia present, and then adding rather more than the calculated quantity of silver nitrate dissolved in water. No precipitate was formed, but, on slowly concentrating the solution in a dark room at a moderately low temperature, colourless needles separated. These were collected with aid of the pump, quickly washed with cold distilled water, in which they are rather soluble, and dried in a vacuum over sulphuric acid. The salt must be kept in a dark place, as it is rather readily acted on by light.

On analysis the following numbers, corresponding with the formula  $C_7H_{10}O_2NAg$ , were obtained.

	Silver.	Carbon.	Hydrogen.
Found . . . . .	43.90, 43.86	33.20	4.11 per cent.
Calculated. . .	43.55	33.89	4.03 „

*Acetyl Derivative*,  $COOH \cdot C(CH_3)_2 \cdot C(CH_3)(CN) \cdot COCH_3$ .—A small quantity of the acid was heated for 10 hours with excess of acetic anhydride in a small reflux apparatus on a sand bath. After the excess of acetic anhydride had been distilled off under a pressure of 200 mm., the receiver was changed, when a colourless oil distilled over at a temperature of  $240^\circ$ ; this, on cooling, solidified to a crystalline mass melting at  $60$ – $63^\circ$ . It is very soluble in acetic anhydride, but it may be obtained in beautiful colourless crystals by allowing an acetic anhydride solution slowly to concentrate in a vacuum over solid potash. It may be recrystallised from hot light petroleum, and, when pure, melts sharply at  $67^\circ$ .

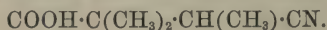
On analysis, it gave the following numbers



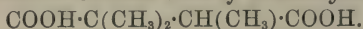
	Carbon.	Hydrogen.	Nitrogen.
Found .....	58.7	7.29	7.89 per cent.
Calculated ( $C_9H_{13}O_3N$ ) ...	59.01	7.10	7.65 „

On warming the acetyl derivative for a few minutes with concentrated hydrochloric acid, it dissolves, and, on cooling, the solution deposits long needles of the original acid, melting at  $126^\circ$ .

*The Constitution of the Acid.*—This was determined by boiling it for several hours in a reflux apparatus with concentrated hydrochloric acid; on cooling, white crystals of trimethylsuccinic acid were deposited, which, after recrystallisation, melted at  $150^\circ$  (see B). The filtrate was found to contain ammonium chloride. These reactions show that the acid has the constitutional formula



B. *The Insoluble Calcium Salt of Trimethylsuccinic acid,*



This calcium salt (B) was decomposed by dissolving it in hot, strong hydrochloric acid; on allowing the solution to cool, a mass of hard greyish-white crystals separated, which, when collected and dried on a porous plate, melted at  $138$  to  $142^\circ$ , but on recrystallisation from concentrated hydrochloric acid the melting point was raised to  $145^\circ$  to  $149^\circ$ . To further purify the acid, it was dissolved in hot water, a slight excess of dilute ammonia added, and the acid again precipitated as calcium salt by boiling with excess of calcium chloride. The calcium salt was collected, washed well with water, and the acid again regenerated by boiling with concentrated hydrochloric acid. The filtered solution, on standing, deposited perfectly white, hard crystals, which, after being dried first on a porous plate and then at  $100^\circ$ , melted sharply at  $151$ – $152^\circ$ . On analysis the acid gave the following numbers:—

	Found.	Calculated for $C_7H_{12}O_4$ .
Carbon .....	52.47	52.50 per cent.
Hydrogen .....	7.23	7.50 „

Trimethylsuccinic acid is fairly soluble in cold water, but almost insoluble in cold concentrated hydrochloric acid. In warm benzene it is very readily soluble, but only sparingly in hot, and quite insoluble in cold light petroleum. It readily dissolves in alcohol and chloroform.

Dr. Walker has kindly determined the dissociation constant of this acid for us. He obtained the value  $K = 0.0302$ , which agrees closely with the number  $K = 0.0304$  given by Auwers (*Ber.*, 1895, 28, 265).

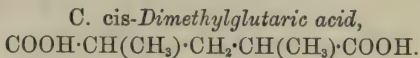
*Anhydride of Trimethylsuccinic acid.*—In order to prepare this, 4 grams of the acid were heated on a sand bath for six hours with excess of acetic anhydride in a small flask, into which a condensing tube was ground. The contents of the flask were then transferred to a small distilling flask, and after the excess of acetic anhydride had been distilled off under a pressure of 200 mm., the receiver was changed and the residual oil distilled over. As the colourless distillate still contained a small quantity of acetic anhydride, it was allowed to stand on a watch-glass in a vacuum over solid potash for two or three days; beautiful colourless crystals gradually formed, which, after drying on a porous plate in a vacuum, melted sharply at  $38\cdot5^\circ$ . On analysis, the following numbers were obtained corresponding with those required for the anhydride of trimethylsuccinic acid.

	Found.	Calculated for $C_7H_{10}O_3$ .
Carbon .....	58.79	59.15 per cent.
Hydrogen.....	6.95	7.00 „

On dissolving a portion of the anhydride in a little hot hydrochloric acid, and allowing the solution to cool, it deposited white crystals of the original trimethylsuccinic acid melting at  $150^\circ$ .

We may here remark that in his recent paper (*Ber.*, 1895, 28, 263), Auwers describes this anhydride as melting at  $31^\circ$ , which is also the same melting point as that observed by Helle (*Inaug. Diss.*, Bonn, 1893). Neither of these investigators appear to have obtained it quite pure.

The results we have thus recorded show that the acid from the insoluble calcium salt is probably identical with the trimethylsuccinic acid described by Zelinsky as melting at  $140$ — $141^\circ$ . It must also be the same as the acid described by Helle as melting at  $131^\circ$  and yielding a very insoluble calcium salt and an anhydride melting at  $31^\circ$ ; and, lastly, the same as the acid recently described by Auwers as melting at  $147$ — $148^\circ$ , and giving an anhydride melting at  $31^\circ$ .



We were at first inclined to think that this acid was the same substance as the needles melting at nearly the same temperature (see (A)). However, on mixing as nearly as possible equal quantities of the two, and making a melting-point determination, we found that the mixture began to melt at  $90^\circ$ , and continued to do so until the thermometer rose to  $105^\circ$ ; this showed that the two acids were different; we subsequently found that they yielded different compounds when treated with acetic anhydride, and, finally, that whereas the needles

contained nitrogen, the other substance did not. The acid appeared to have the same properties as the dimethylglutaric acid described by Zelinsky (*Ber.*, 1889, **22**, 2823) as melting at  $128^{\circ}$ , and the following analytical results bore out that conclusion.

	Found.	Calculated for $C_7H_{12}O_4$ .
Carbon .....	52.73	52.50 per cent.
Hydrogen.....	7.55	7.55 „

It is moderately soluble in water, but almost insoluble in cold concentrated hydrochloric acid. In benzene it is rather soluble, but not so readily as the acid D; it is insoluble in light petroleum, but readily soluble in alcohol and chloroform.

*Anhydride of cis-Dimethylglutaric acid.*—A small quantity of the acid was heated with excess of acetic anhydride on a sand bath for three hours in a small reflux apparatus; the contents of the flask were then transferred to a small distilling flask, and the excess of acetic anhydride distilled off under reduced pressure (100 mm.). The receiver having then been changed, the pressure was further reduced to 40 mm., and the distillation continued, when the anhydride of *cis*-dimethylglutaric acid passed over at  $180^{\circ}$  to  $185^{\circ}$  as a colourless oil, which solidified on cooling. It was recrystallised from acetic anhydride, and the crystals dried on a porous plate in a vacuum over solid potash. It melted sharply at  $93.5^{\circ}$ . On redissolving it in hot hydrochloric acid and allowing the solution to cool, crystals of the original acid were deposited, which, on drying, melted at  $128.5^{\circ}$ . This indicates that the dimethylglutaric acid melting at  $128^{\circ}$  is the *cis*-modification.

Dr. Walker kindly determined the dissociation constant of this acid and found  $K = 0.0056$ .

#### D. *The Acid melting at $105^{\circ}$ to $107^{\circ}$ .*

This acid is doubtless identical with the compound Zelinsky obtained by the same reaction as ourselves, and which he found melted at  $100^{\circ}$  to  $101^{\circ}$ , and had a dissociation constant  $K = 0.0063$  (*Ber.*, 1891, **24**, 459). He, however, still maintains that it is a trimethylsuccinic acid, whereas we shall show that it must be a dimethylglutaric acid. We may here remark that it is exceedingly difficult to get this substance quite free from the higher melting *cis*-dimethylglutaric acid, and it does not usually melt quite sharply, but this is a point to which we shall have occasion to refer again. The acid is readily soluble in benzene, but much less so if a little light petroleum be added to the solution; in light petroleum itself, it is almost insoluble. It is very soluble in water, but only sparingly in concentrated hydro-

chloric acid, it is, however, rather more soluble in this last named liquid than *cis*-dimethylglutaric acid.

The acid on analysis gave the following numbers :—

	Found.	Calculated for $C_7H_{12}O_4$ .
Carbon .....	52.10	52.50 per cent.
Hydrogen.....	7.34	7.50 „

The dissociation constant of this acid determined by Dr. Walker is  $K = 0.0057$ .

*Conversion into the Anhydride.*—The acid was heated with excess of acetic anhydride in a reflux apparatus for four hours on a sand bath. The acetic anhydride was first removed by distillation under reduced pressure, and then the anhydride of dimethylglutaric acid passed over; it is a colourless oil, which solidified to a white mass on cooling, and, after recrystallisation from acetic anhydride, and drying on a porous plate in a vacuum over potash melted at 93—94°.

The crystals, on analysis, gave the following numbers.

	Found.	Calculated for $C_7H_{10}O_3$ .
Carbon .....	59.13	59.15 per cent.
Hydrogen.....	6.98	7.00 „

The anhydride was converted into the acid by dissolving it in hot concentrated hydrochloric acid, the solution on standing depositing white crystals melting at 128.5°.

Thus it will be seen that the two acids described under C and D, melting at 128.5° and 105—107° respectively, yield the *same* anhydride, melting at 93—94°, which with water yields the acid of higher melting point. There can therefore be no doubt but that Zelinsky is wrong in calling the acid (m. p. 100—101°) which he obtained a trimethylsuccinic acid.

As stated in the introduction to this paper, Auwers has recently published experiments calling in question the homogeneous character of this acid (*Ber.*, 1895, **28**, 269). He regards it as a mixture in molecular proportion of the acid we have described as *cis*-dimethylglutaric acid, melting at 127°, and a new dimethylglutaric acid (*trans*-), melting at 140° to 141°. He separated these acids, either by means of their calcium salts or by treatment with acetyl chloride; in the latter case the *cis*- acid present is readily converted into the anhydride in the cold, whereas the *trans*- acid is unchanged, acetyl chloride converting it into the anhydride only after continued heating of the mixture in a sealed tube. Up to the appearance of Auwers' last paper, the authors never found anything which threw doubt upon the homogeneous nature of their 105° acid. It is true that it did not melt quite sharply, but this they always thought was due to



the presence of a very small amount of the *cis*- acid, the last traces of which are very difficult to remove. The authors have done much work on this acid, which so far has yielded some very remarkable results, differing very materially from those recently published by Auwers; probably when the latter publishes a more detailed account of his work the discrepancies between their results and his will be explained, but they are subjecting this acid to a thorough examination, and must reserve the results for a future communication.

*Preparation of Trimethylsuccinic acid by Bischoff's Reaction.*

Bischoff and Mintz (*Ber.*, 1890, **23**, 647), by the action of ethylic  $\alpha$ -bromisobutyrate on the sodium compound of ethylic methylmalonate in alcoholic solution at 100°, and subsequent hydrolysis of the ethereal salt produced, obtained as principal product an acid melting at 105°; this they at first described as trimethylsuccinic acid, but afterwards came to the conclusion that it was a dimethylglutaric acid. A little later Bischoff (*Ber.*, 1891, **24**, 1041) found that by conducting the reaction in xylene solution at 180° he obtained, besides this dimethylglutaric acid, a trimethylsuccinic acid melting at 139.5°. Helle (*Inaug. Diss.*, Bonn, 1893), on repeating this synthesis, obtained an acid melting at 131°, and yielding an anhydride melting at 31°. He also found the same acid was formed by the dry distillation of camphoronic acid. The question at once arises are these acids, prepared by Bischoff and Helle, identical with the trimethylsuccinic we have described already, and if not, are they trimethylsuccinic acids at all? To decide this point, we repeated their work, and found that one of the acids formed melted at 151°, and was in all respects identical with the trimethylsuccinic acid we prepared by Zelinsky's method.

*Interaction of Ethylic  $\alpha$ -Bromisobutyrate and Ethylic Sodiomethylmalonate in Xylene Solution at 180°.*—One hundred and three grams of ethylic methylmalonate were dissolved in 150 c.c. of xylene contained in a round-bottomed flask, and 13.3 grams of sodium in the form of wire added in two portions. The sodium gradually dissolved in the cold, but much more rapidly if the flask was gently warmed on a sand bath, and at the same time the sodium compound of ethylic methylmalonate separated as a brownish, pasty mass. As soon as the sodium had completely disappeared, the flask was cooled, 106 grams of ethylic  $\alpha$ -bromisobutyrate were carefully added, and the whole boiled in a reflux apparatus in an oil bath for two days. As soon as the mixture had acquired a neutral reaction, it was poured into water, and the oily layer which separated mixed with ether; the ethereal solution, washed first with dilute sodium carbonate solution

and then with water, was dried over calcium chloride, and the ether distilled off. The residue was now distilled under a pressure of 45 mm., when, between 90° and 100°, a large quantity of xylene came over, and then between 140° and 155°, some 20 grams of oil, mostly unchanged ethylic methylmalonate. The receiver was now changed, and the fractionation continued; the temperature rose somewhat rapidly to 170°, and from this point very slowly to 200°, most of the oil, however, seemed to distil over at two temperatures, namely, 185° and between 195° and 200°. The fraction passing over between 170° and 200° amounted to about 55 grams, and about 20 grams of a residue of higher boiling point was left in the retort.

*Hydrolysis of the Oil boiling between 140° and 200°.*—The two fractions obtained above, boiling at 140—155° and 155—200° respectively, were united and added to 90 grams of potassium hydroxide dissolved in alcohol. The mixture was then heated in a reflux apparatus for six hours on a water bath, during which time a quantity of potassium salts separated. The contents of the flask were then poured into water, and after the solution had been evaporated in a large basin on the water bath until all the alcohol had volatilised, the liquid was acidified with hydrochloric acid, and the acids extracted by repeatedly shaking with pure ether. The ethereal solution was dried over calcium chloride, the ether distilled off, and the residual oil heated at 200° until all evolution of carbonic acid had ceased. On distilling the thick oily residue under a pressure of 30 mm., a considerable portion, *A*, passed over between 130° and 200°, the thermometer rising steadily all the time; this contained a good deal of propionic acid. The receiver was changed at 200°, and the oil, *B*, passing over between 200° and 250°, was collected; these two fractions were then worked up separately.

*Fraction A (130—200°).*—This smelt strongly of propionic acid, but on adding dilute ammonia in excess a large amount of oil remained undissolved in the cold, although on boiling everything went into solution. The liquid was then diluted and boiled with animal charcoal, filtered, and to the filtrate, which was pale yellow, a solution of 30 grams of calcium chloride was added. On boiling the liquid on a sand bath, a large quantity of an insoluble calcium salt separated, which was collected with the aid of the pump. The filtrate contained the more soluble calcium salt of an acid melting at 104—107°.

*Fraction B (200—250°).*—This was treated in exactly the same way as *A*, but only a very small quantity of the insoluble calcium salt was obtained, this fraction largely consisting of the acid of lower melting point.

*Decomposition of the Insoluble Calcium Salt.*—The calcium salt,

dissolved in excess of hot and strong hydrochloric acid, yielded colourless crystals on cooling, which, after being separated from the mother liquor and dried, melted at  $140-148^\circ$ . The acid was purified by redissolving it in ammonia, reprecipitating as calcium salt, and decomposing this with hot hydrochloric acid, &c. In this way the acid was obtained as a colourless, crystalline powder, melting at  $150^\circ$ ; on recrystallisation from hydrochloric acid its melting point rose to  $151^\circ$ .

The acid gave the following numbers on analysis.

	Found.	Calculated for $C_7H_{12}O_4$ .
Carbon .....	52.41	52.50 per cent.
Hydrogen.....	7.72	7.50 „

It was in every respect identical with the trimethylsuccinic acid prepared by Zelinsky's method, melting at  $152^\circ$ .

*Owens College Chemical Laboratory,  
Manchester.*

NOTE ON THE  $\alpha\alpha_1$ -DIMETHYLGLUTARIC  
ACIDS.

BY

WILLIAM ARTHUR BONE

AND

WILLIAM HENRY PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1896.]





### Note on the $\alpha\alpha_1$ -dimethylglutaric acids.

By WILLIAM ARTHUR BONE, and WILLIAM HENRY PERKIN, Jun.

IN a paper published last year (Trans., 1895, **67**, 416), the authors described as  $\alpha\alpha_1$ -dimethylglutaric acids two acids melting at  $127^\circ$  and  $105\text{--}107^\circ$  respectively, obtained, together with trimethylsuccinic acid (m. p.  $152^\circ$ ), by the hydrolysis of the product of the action of ethylic  $\alpha$ -bromisobutyrate on the sodium derivative of ethylic  $\alpha$ -cyanopropionate, in alcoholic solution. In the same communication, they stated that Auwers and Thorpe (*Ber.*, 1895, **28**, 623) had shown that the acid melting at  $105\text{--}107^\circ$  was not a homogeneous substance, but a mixture in molecular proportion of *cis*- and *trans*- $\alpha\alpha_1$ -dimethylglutaric acids, melting at  $127^\circ$  and  $140\text{--}141^\circ$  respectively, but up to the time of the publication of their results the authors have not been able to confirm this opinion. Since that time, however, Auwers and Thorpe have published fuller details of their work (*Annalen*, 1895, **285**, 310), and the authors have accordingly subjected the acid in question to a further examination, with the result that they are able to substantiate the conclusions of these investigators.

The acid melting at  $105\text{--}107^\circ$  is in many respects a remarkable substance; it may be recrystallised from various solvents, such as benzene or concentrated hydrochloric acid, without any change in its melting point. The authors fractionally crystallised the normal calcium salt, obtained by adding excess of calcium chloride to a dilute solution of the ammonium salt, and on regenerating the acids from the successive fractions by separately dissolving them in concentrated hydrochloric acid, they were found to melt within  $2^\circ$  of the original

acid. No separation could be effected by this method. Auwers and Thorpe found, however, that if the acid calcium salt, prepared by adding the calculated quantity of calcium carbonate to an aqueous solution of the acid, was fractionally crystallised, two calcium salts could be obtained, one being very much less soluble than the other. On regenerating the acids, the more insoluble salt yielded *trans*-dimethylglutaric acid, melting at 140—141°, and the other *cis*-dimethylglutaric acid, melting at 127°.

The authors are able to confirm this result, and have resolved the acid, melting at 105—107°, into its two constituents, by the following method, also due to Auwers and Thorpe; it depends on the fact that *cis*-dimethylglutaric acid readily yields an anhydride on treatment with acetyl chloride, whilst the *trans*-acid remains unchanged. The acid, melting at 105—107°, was mixed with half its weight of acetyl chloride in a test-tube, the mixture gently warmed for about 10 minutes, until the evolution of hydrogen chloride had ceased, and the substance had completely dissolved, and the solution was then left in a vacuum over solid potassium hydroxide, until the whole of the acetyl chloride had volatilised. The solid residue thus obtained was quickly washed with benzene, whereby the anhydride of the *cis*-acid was completely removed, leaving behind the unchanged *trans*-acid, which, after recrystallisation from hot, hydrochloric acid, was found to melt at 140—141°. On leaving the filtrate in a warm place until the benzene had evaporated, an oily liquid was left, which, on long standing, became semi-solid; it dissolved readily in hot, concentrated hydrochloric acid, and on cooling the solution crystals of *cis*-dimethylglutaric acid, melting at 125—127°, separated. The mother liquor was extracted with pure ether, and after drying the ethereal solution over calcium chloride and distilling off the ether, a residue was left, which was recrystallised from benzene; in this way a small quantity of an acid, melting between 100° and 110°, was obtained. On grinding together equal portions of *cis*- and *trans*-dimethylglutaric acids in a mortar, a substance was obtained which had an almost constant melting point, namely, 104—108°, resembling in every way the acid melting at 105—107°, which the authors described in their former paper.

Owens College, Manchester.

*CIS- AND TRANS-METHYLISOPROPYLSUCCINIC*  
*ACID.*

BY

WILLIAM HENRY BENTLEY,  
WILLIAM HENRY PERKIN, JUN.,  
AND  
JOCELYN FIELD THORPE.

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[From the Transactions of the Chemical Society, 1896.]



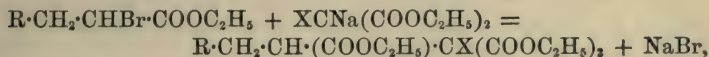


# Cis- and trans-methylisopropylsuccinic acid.

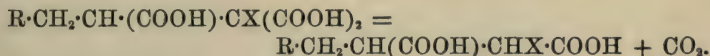
By WILLIAM HENRY BENTLEY, WILLIAM HENRY PERKIN, jun., and  
JOCELYN FIELD THORPE.

THE action of the ethereal salts of  $\alpha$ -bromo-acids of the fatty series on the sodium compounds of ethylic malonate and its derivatives may take place in two different ways.

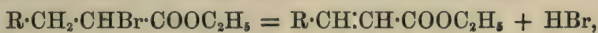
1. The action may proceed directly with the simple separation of sodium bromide, thus:—



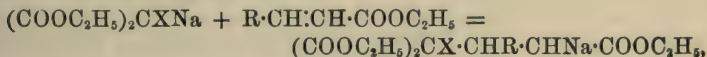
forming an ethereal salt of a tribasic acid, which, on hydrolysis and subsequent elimination of  $\text{CO}_2$ , yields a derivative of succinic acid, thus:—



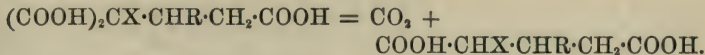
2. The reaction is an indirect one. In this case an unsaturated ethereal salt is first produced by the removal of hydrogen bromide,



and this unsaturated ethereal salt then condenses with the sodium derivative employed, as follows,



yielding a sodium derivative of an ethereal salt from which the corresponding tribasic acid may be isolated by hydrolysis. This tribasic acid then readily decomposes on heating with formation of a derivative of glutaric acid,



The direction in which the action proceeds depends generally on the conditions of the experiment; thus, when ethylic  $\alpha$ -bromisubutyrate is digested with ethylic methyl malonate in alcoholic solution (Bischoff and Mintz, *Ber.*, 1890, **23**, 649), an ethereal salt of the formula  $(\text{COOC}_2\text{H}_5)_2\text{C}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$  is produced, from which, by hydrolysis and elimination of  $\text{CO}_2$ , the two symmetrical dimethylglutaric acids are obtained; whereas if the experiment be performed in xylene solution at  $200^\circ$ , the action proceeds directly with separation of sodium bromide and formation of ethylic trimethylethanetricarboxylate,  $(\text{COOC}_2\text{H}_5)_2\text{C}(\text{CH}_3)\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOC}_2\text{H}_5$ ,

from which trimethylsuccinic acid is readily produced (Bischoff, *Ber.*, 1891, **24**, 1078; Bredt and Helle, *Inaugural Dissert.*, Bonn, 1893, 31; Auwers, *Annalen*, 1895, **285**, 260 and 301).

During some experiments on the action of ethylic bromomethylisopropylacetate,  $(\text{CH}_3)_2\text{CH}\cdot\text{CBr}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$ , on the sodium derivative of ethylic malonate, on which one of us has been engaged for some time, it was found to be exceedingly difficult to decide whether the substances obtained were derivatives of succinic, or of glutaric acid,\* and, in order to throw some light on this point, a series of experiments on the action of the next lower homologue, namely, ethylic bromisopropylacetate (ethylic  $\alpha$ -bromisovalerate) on the sodium derivative of ethylic methylmalonate were instituted, with the results described in this communication.

If this decomposition proceed as indicated in equation 1, the end product would be methylisopropylsuccinic acid,



if, however, hydrogen bromide were eliminated, and subsequent condensation took place, the end product would be trimethylglutaric acid,  $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ , and it would be easy to distinguish between these substances, since, in the former case, the acid would contain two asymmetric carbon atoms, and be capable, therefore, according to the Le Bel-van't Hoff theory, of existing in two distinct inactive modifications, namely, *cis*,  $\begin{array}{c} \text{C}_3\text{H}_7\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{CH}_3\cdot\text{CH}\cdot\text{COOH} \end{array}$  and

*trans*,  $\begin{array}{c} \text{C}_3\text{H}_7\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{COOH}\cdot\text{CH}\cdot\text{CH}_3 \end{array}$ , methylisopropylsuccinic acid; whereas the above trimethylglutaric acid, containing only one asymmetric carbon atom, is capable, according to the same theory, of existing in one inactive modification only.

The action of ethylic  $\alpha$ -bromisovalerate on the sodium derivative of ethylic methylmalonate was first carried out in boiling xylene solution in the usual manner, the purified ethereal salt obtained was hydrolysed, and the acid produced heated at  $200^\circ$  until all evolution of carbonic anhydride had ceased.

From the product, two well characterised acids melting at  $174\text{--}175^\circ$  and  $124\text{--}125^\circ$ , were isolated, which, from the study of their behaviour, were clearly shown to be stereoisomeric; these acids, therefore, are evidently the *cis*- and *trans*-methylisopropylsuccinic acids, which are formed by the direct action of ethylic  $\alpha$ -bromisovalerate on the sodium derivative of ethylic methylmalonate, according to equation 1.

*Cis*-Methylisopropylsuccinic acid differs from the *trans*-acid in being

\* It is hoped that the results of these experiments, which are complete, will be ready for publication shortly.

readily volatile with steam when heated with a 50 per cent. solution of sulphuric acid. It melts at 125—126°, and, when treated with hydrochloric acid, is partially converted into the *trans*-modification melting at 174—175°. When heated with acetic anhydride, or when distilled, the *cis*-acid yields a liquid anhydride, and this, on treatment with water, is reconverted into the original acid.

The *cis*-anilic acid, 
$$\begin{array}{c} (\text{CH}_3)_2\text{CH}\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{CH}_3\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5 \end{array} \quad (?)$$
, melts at 160°, and is different from the anilic acid of the *trans*-acid, although both yield the same anil when heated at 200°.

*Trans-methylisopropylsuccinic acid* is much less soluble in water than the *cis*-acid; it melts at 174—175°, and when heated with hydrochloric acid at 180°, is partially converted into the *cis*-acid.

When distilled under reduced pressure, or heated with acetic anhydride, the *trans*-acid yields a solid anhydride melting at 46°, which by treatment with water is reconverted into the same acid. If, however, this anhydride be boiled in a reflux apparatus for some time under ordinary pressure, and then distilled, the distillate is found to consist of the *cis*-anhydride; the conversion of the *trans*- into the *cis*-acid being complete under these circumstances. The *trans*-anhydride, on treatment with aniline, gives the anilic acid of the *trans*-acid, and this, when heated at 200°, yields the anil of the *cis*-acid.

We next studied the action of ethylic  $\alpha$ -bromisovalerate on the sodium derivative of ethylic methylmalonate in alcoholic solution, and in this case again, curiously enough, working up the product in the way described in the body of the paper, we were only able to isolate *cis*-methylisopropylsuccinic acid, the *trans*-modification which should have been formed being apparently converted into the *cis*-acid under the conditions of hydrolysis employed in this particular instance.

Lastly, in order that there might be no doubt as to the constitution of these acids, we have prepared them in the following way.

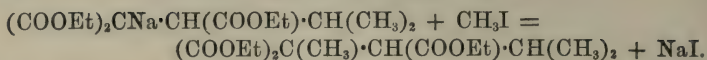
In the first place, the sodium derivative of ethylic malonate was digested with ethylic  $\alpha$ -bromisovalerate, when a good yield of an ethereal salt was obtained, which has already been described by Roser (*Annalen*, 1883, **220**, 277), and which is undoubtedly ethylic isopropylethanetricarboxylate,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{COOC}_2\text{H}_5)\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$ . In order to be certain of the constitution of this ethereal salt, it was hydrolysed, and the tribasic acid formed heated at 200°, whereby it was converted into isopropylsuccinic acid,



a result which confirms Roser's experiments.

The ethylic isopropylethanetricarboxylate was now treated with sodium and methylic iodide in alcoholic solution,



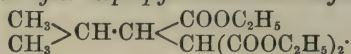


The ethereal salt thus formed was identical with that obtained in the previous experiments, since, on hydrolysis and subsequent elimination of carbon dioxide, a mixture of acids was obtained from which *cis*- and *trans*-methylisopropylsuccinic acid, melting at 174—175° and 124—125° respectively, were readily isolated. These acids differed in no respect from those produced in the manner previously described.

The latter method gives by far the best yield of these acids; it is therefore placed first in this paper, and described in most detail.

### EXPERIMENTAL PART.

#### I. *Ethylic Isopropylethanetricarboxylate*,



In preparing this substance, 23 grams of sodium were dissolved in 250 grams of absolute alcohol and 160 grams of ethylic malonate added, when the sodium derivative separated as a white, gelatinous precipitate. The flask containing the mixture was then connected with a reflux condenser, heated on the water bath, and 209 grams of ethylic  $\alpha$ -bromisovalerate added in small portions at a time to the boiling solution. The action was not violent, although sodium bromide separated immediately on adding the bromisovalerate; the boiling was continued for three hours, after which the product was neutral. The alcohol was, as far as possible, distilled off, this being most quickly and completely effected by placing the flask in the boiling water bath, bumping being prevented by suspending a piece of string from the neck of the flask, so as to hang in the boiling liquid.

When the alcohol had ceased to come over, the residue in the flask was mixed with water, the oil separated, the aqueous liquor extracted four times with ether, the ethereal solution dried over calcium chloride, and the ether distilled off. The oily product was then fractionated under reduced pressure (37 mm.); a small portion boiled below 200°, but the chief portion came over between 180° and 182°. The weight of this fraction was 186 grams, or 66 per cent. of the theoretical yield of ethylic isopropylethanetricarboxylate.

0.1510 gave 0.3209  $\text{CO}_2$  and 0.1155  $\text{H}_2\text{O}$ . C = 57.96; H = 8.49.

$\text{C}_{14}\text{H}_{24}\text{O}_6$  requires C = 58.33; H = 8.33 per cent.

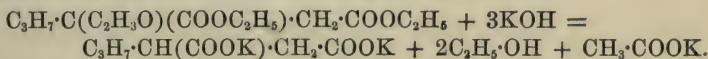
In order to prove that this ethereal salt has the constitution represented by the formula at the head of this section, 20 grams of the

pure substance were hydrolysed by boiling with an alcoholic solution of potash for two hours, evaporating the product three times with water, acidifying, and extracting several times with ether; after drying over calcium chloride and evaporating the ether, the oily acid was heated at  $200^{\circ}$  until the evolution of gas had ceased, and the product, which rapidly solidified and melted indefinitely at  $90\text{--}110^{\circ}$ , was recrystallised from hydrochloric acid until the melting point became constant at  $116\text{--}117^{\circ}$ .

0.2297 gave 0.4408  $\text{CO}_2$  and 0.1555  $\text{H}_2\text{O}$ .  $\text{C} = 52.33$ ;  $\text{H} = 7.53$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.52$ ;  $\text{H} = 7.52$  per cent.

A careful examination of this acid proved conclusively that it is identical with the isopropylsuccinic acid obtained by Hlasiwetz and Grabowski (*Annalen*, 1868, **145**, 207), from the fusion of camphoric acid with potash, and which Roser (*Annalen*, 1883, **220**, 272) has shown to be identical with the acid obtained by the hydrolysis of ethylic isopropylacetosuccinate with potash,



Not only do the melting points of these acids coincide, but on comparing the anilic acid produced from the acid obtained by us with that prepared from a sample of isopropylsuccinic acid, which had been obtained by fusing camphoric acid with potash, they both melted at  $145^{\circ}$ , and were identical in all respects.

This anilic acid, which does not appear to have been previously prepared, is readily obtained by mixing isopropylsuccinic anhydride with aniline in benzene solution; it crystallises from a mixture of light petroleum and ethylic acetate in large, glistening plates melting at  $145^{\circ}$ . A nitrogen determination gave the following figures.

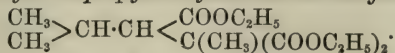
0.1991 gave 9.9 c.c. moist nitrogen at  $12^{\circ}$  and 760 mm.  $\text{N} = 6.00$ .

$\text{C}_{13}\text{H}_{17}\text{NO}_3$  requires  $\text{N} = 5.96$  per cent.

On heating this anilic acid in a sulphuric acid bath at  $200^{\circ}$  for half an hour, it loses water, and is converted into the anil.

This compound crystallises from light petroleum ( $80\text{--}100^{\circ}$ ) in microscopic needles melting at  $213^{\circ}$ . The same substance was obtained both from the anilic acid prepared from the synthetically produced isopropylsuccinic acid, and from that prepared from the isopropylsuccinic acid from camphoric acid.

*Ethylic Isopropylmethylethanetricarboxylate,*



This was prepared as follows. 13.3 grams of sodium were dissolved in 133 grams of absolute alcohol, and 166 grams of ethylic

isopropylethanetricarboxylate added; the mass became yellow, but no separation of the sodium derivative was observed. The flask was fitted with a reflux condenser, the solution cooled, and 95 grams (an excess) of methylic iodide added in small portions at a time through the condenser tube; the action was very violent, the temperature rising rapidly until the liquid boiled vigorously. In order to complete the action, the mixture was heated on the water bath for two hours, when it was found to be neutral; the product was then treated as usual, the alcohol being distilled off, water added, and the oil extracted with ether. This oil, which was deep red, owing to the presence of free iodine, was fractionated under reduced pressure (80 mm.), when the principal portion distilled between  $200^{\circ}$  and  $210^{\circ}$ ; the weight of this fraction was 144 grams, or 83 per cent. of the theoretical quantity. An analysis gave the following results.

0.2197 gave 0.4818  $\text{CO}_2$  and 0.1707  $\text{H}_2\text{O}$ . C = 59.81; H = 8.63.

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires C = 59.60; H = 8.60 per cent.

*Hydrolysis of Ethylic Isopropylmethylethanetricarboxylate by means of Alcoholic Potash.*

The pure ethereal salt (144 grams) was boiled in a reflux apparatus with an alcoholic solution of one and a half times the calculated quantity of potash for four hours, the product diluted with water, and evaporated on a water bath to a small bulk until quite free from alcohol. On acidifying this potassium salt with hydrochloric acid, it was noticed that there was a marked evolution of carbon dioxide, which indicated that the tribasic acid, which should result from the direct hydrolysis of the ethereal salt, had either during the hydrolysis or on acidifying with hydrochloric acid, been at least partially decomposed into dibasic acids with loss of carbon dioxide, and this was afterwards found to be the case. On standing, an oil, which rapidly solidified, separated on the surface of the strongly acid liquid. The whole was then transferred to a separating funnel and extracted seven times with pure ether, the ethereal solution dried over calcium chloride, filtered, and evaporated, when a slightly yellowish oil remained, which partially solidified on standing. This product was heated in an oil bath at  $200^{\circ}$ , but only a small quantity of carbon dioxide was evolved, confirming the conclusion arrived at above, that the tribasic acid had been for the most part already decomposed. The light brownish residue which contained *cis*- and *trans*-methylisopropylsuccinic acids was then treated by the method described in the next paragraph.

*Separation of cis- and trans-Methylisopropylsuccinic acid.*

*Method I.*—The method used by us for the separation of these



acids is similar to that employed by Hell (*Ber.*, 1877, **10**, 2229) for the isolation of diisopropylsuccinic acid and of tetramethylsuccinic acid, namely, distillation in steam from a 50 per cent. solution of sulphuric acid.

The mixed acids were placed in a conveniently large flask, together with a 50 per cent. solution of sulphuric acid, and distilled in a current of steam, when a large quantity of an oil heavier than water passed over; at the end of two hours, as no more oil passed over and the distillate was only slightly acid, the distillation was stopped.

(a.) *Treatment of the Residue in the Distilling Flask.*—On cooling, a large quantity of a crystalline substance separated from the dark brown sulphuric acid solution; this was collected, and after being washed with water, it melted roughly at 130—160°; crystallisation from water, however, at once raised the melting point to 160—170°, and subsequently to 174—175°, where it remained constant; the quantity of this substance was 18 grams.

The filtrate from the crystals was extracted four times with ether, and the ethereal solution dried and evaporated; the thick, syrupy residue had only partially solidified after standing over sulphuric acid for two days in a vacuum; on treatment with cold benzene, this was readily separated into two parts.

1. An *insoluble*, white, crystalline mass melting roughly at 89—104°.

2. A *soluble* portion which was deposited as an oil on evaporating the benzene; the quantity of this was, however, small, and as all attempts to obtain a crystalline substance from it were unsuccessful, it was not further investigated. It is worthy of remark, however, that on dissolving this oil in water and saturating the solution with gaseous hydrogen chloride, the substance was reprecipitated as an oil, and not in a crystalline condition.

In order to purify the crystalline substance insoluble in cold benzene, it was treated with boiling benzene and filtered from a small quantity of insoluble inorganic matter; on cooling, needle-shaped crystals separated which, after being washed with benzene, melted at 95—110°, but, on repeated recrystallisation from water, the melting point rose to 117—118°, where it remained constant.

The quantity of this acid, which was evidently isopropylsuccinic acid, was only about 1 gram.

(b.) *Treatment of the Substance Volatile with Steam.*—The steam distillate consisted of a large volume of liquid containing oily drops at the bottom, which dissolved on the addition of excess of potash and warming; the clear solution thus obtained was evaporated in a porcelain dish to a small bulk, acidified with hydrochloric acid,



extracted six times with ether, and the ethereal solution dried over calcium chloride and evaporated, when a very small quantity only of an oil was left which solidified on standing; on recrystallisation from water, an acid was obtained melting at  $174^{\circ}$ — $175^{\circ}$ , evidently identical with the acid of the same melting point already obtained as described above; the quantity was, however, very small and hardly sufficient for a melting point determination.

Considering the large quantity of original acid employed, only small amounts of pure substance had been extracted by ether, and it seemed likely, therefore, that an acid was contained in the steam distillate, which, owing to its great solubility in water, was not capable of being easily extracted by agitation with ether; this proved to be the case, for on evaporating the mother liquor (which had previously been made alkaline by the addition of potash) to dryness on the water bath, adding excess of concentrated hydrochloric acid, and again extracting six times with ether, a large quantity of a solid substance was obtained melting at about  $110$ — $120^{\circ}$ . This could not be recrystallised in the ordinary way owing to its great solubility; but when it was dissolved in a little water, and the solution saturated with hydrogen chloride, the pure substance, on standing, separated almost completely in microscopic needles melting at  $125$ — $126^{\circ}$ . The yield of this acid was 30 grams from the 144 grams of ethylic methylisopropylethanetricarboxylate used.

The products of the hydrolysis of the 144 grams of this ethereal salt may therefore be tabulated as follows.

1. An acid (18 grams) melting at  $174$ — $175^{\circ}$ , only very slightly volatile with steam,\* insoluble in hot benzene.
2. An acid (1 gram) melting at  $117$ — $118^{\circ}$ , not readily volatile with steam,\* but easily soluble in hot benzene.
3. An acid (30 grams) melting at  $125$ — $126^{\circ}$ , volatile with steam,\* and readily soluble in hot benzene.

In the following sections, we give a detailed account of the properties of the two acids melting at  $175^{\circ}$  and  $126^{\circ}$  respectively, showing that the former is the *trans*-, the latter the *cis*-methylisopropylsuccinic acid.

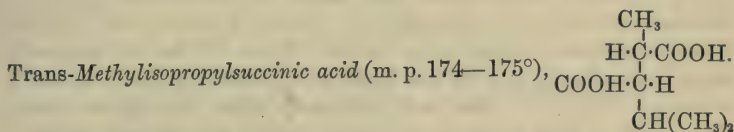
*Method II.*—Although as a method for the rough separation of large quantities of the crude mixed acids, distillation with steam from a 50 per cent. solution of sulphuric acid serves admirably, and yields the *cis*- and *trans*-acids in a tolerably pure form, yet it cannot be advantageously applied when smaller quantities have to be dealt with.

Repeated recrystallisation of the crude mixture of acids from water fails to produce an acid of higher melting point than  $170$ — $173^{\circ}$ ,

\* From a 50 per cent. solution of sulphuric acid.

and it is therefore almost impossible by these means to obtain a pure *trans*-acid; if, however, the recrystallised product be boiled for a few minutes with benzene, in which it is almost insoluble, filtered while hot, washed with warm benzene, and the product thus obtained subsequently recrystallised from water, long, flat needles of constant melting point, 174—175°, are readily obtained.

Owing to the marked difference in the solubility of the *cis*- and *trans*-acids in water, the *cis*-acid is obtained in a very fair degree of purity on saturating the mother liquors with hydrogen chloride; the product, however, still contains traces of the *trans*-modification, but can easily be purified by treating with cold benzene, filtering, evaporating the filtrate to dryness, and recrystallising the residue thus obtained from hydrochloric acid, as above described.



This acid crystallises from water in long, flat needles, which melt at 174—175°, and decompose at 190° with formation of the anhydride. The following results were obtained on analysis.

0.2272 gave 0.4587 CO<sub>2</sub> and 0.1640 H<sub>2</sub>O. C = 55.00; H = 8.02.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17. H = 8.04 per cent.

*Trans*-methylisopropylsuccinic acid is readily soluble in hot water, ether, and ethylic acetate, but only sparingly in light petroleum and chloroform, almost insoluble in cold water and benzene. The solubility in water was determined by Victor Meyer's method, when it was found that at 18°, 2.6146 grams of water dissolve 0.170 gram of the acid, or 100 parts of water dissolve 0.64 part of the acid at 18°. This acid is, therefore, very sparingly soluble in cold water.

The *silver salt*, C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>Ag<sub>2</sub>, prepared by neutralising a 10 per cent. solution of the acid with a slight excess of ammonia, boiling for some time, concentrating, adding a little water, and then the requisite quantity of silver nitrate solution, gave the following result on analysis.

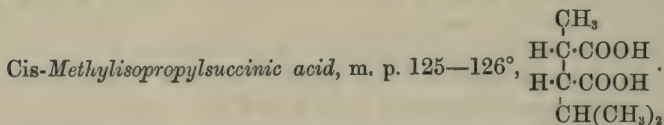
0.2122 gave, on ignition, 0.1181 Ag. Ag = 55.65.

C<sub>8</sub>H<sub>12</sub>Ag<sub>2</sub>O<sub>4</sub> requires Ag = 55.67 per cent.

*Action of Heat on trans-Methylisopropylsuccinic acid.*—When gently boiled for a few minutes under slightly diminished pressure, and then distilled, *trans*-methylisopropylsuccinic acid is converted into an anhydride which, on boiling with water, yields an acid melting from 120—165°, and from which a small quantity of *trans*-acid can

be isolated by crystallisation from water. The mother liquor, when concentrated and saturated with hydrogen chloride, yields a considerable quantity of *cis*-methylisopropylsuccinic acid melting at 125—126°. The presence of the *trans*-acid in this product was at first thought to be due to its having distilled unchanged, but as no carbon dioxide was evolved on heating the distillate with a solution of sodium carbonate, this did not seem probable. Subsequently it was proved, however, that anhydrides of both acids exist, the *trans*-anhydride being only completely converted into the *cis*-modification after repeated distillation under ordinary or slightly reduced pressure.

*Behaviour of trans-Methylisopropylsuccinic acid on heating with Hydrochloric acid at 180°.*—In order to investigate this important point, 3 grams of the pure acid were heated with concentrated hydrochloric acid in a closed tube, at 180°, for eight hours; the crystals which separated on cooling, melted at 120—150°, but on recrystallising and extracting with hot benzene, a quantity of the *trans*-acid, melting at 174—175°, was readily obtained, whilst the mother liquor, on saturation with hydrogen chloride, yielded the *cis*-acid, the two acids being in, apparently, about equal proportions. As, on subsequent investigation, the *cis*-acid, when heated in like manner with hydrochloric acid, yielded a mixture of the two acids, it was inferred that here, as in the cases of the symmetrical  $\alpha$ -dimethylglutaric acids, the hexahydroisophthalic acids, and other similarly constituted acids, a state of equilibrium exists. It is interesting to note that in this case it is quite easy to separate the mixture of the *cis*- and *trans*-acids obtained into its components by means of benzene; and that it does not behave like the mixture of *cis*- and *trans*-dimethylglutaric acids, which can only be separated with very great difficulty (*Annalen*, 1895, 285, 332).



On saturating the aqueous solution of the acid with hydrogen chloride and allowing it to cool, microscopic needles separate, which melt at 125—126°, and decompose at 140°, with formation of the anhydride. The analysis gave the following figures.

0.1135 gave 0.2282 CO<sub>2</sub> and 0.0794 H<sub>2</sub>O. C = 54.83; H = 7.77.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17; H = 8.04 per cent.

*Cis-Methylisopropylsuccinic acid* is readily soluble in all the usual solvents, with the exception of light petroleum, in which it is only



sparingly soluble in the cold; it also dissolves readily in acetyl chloride. The solubility in water, determined by Victor Meyer's method, yielded the following result at 18°. 2.1046 grams of water dissolve 0.0934 gram of the acid, or 100 parts of water dissolve 4.43 parts of the *cis*-acid at 18°, it is, therefore, much more soluble than the *trans*-acid, of which 100 parts of water dissolve only 0.64 part at this temperature.

The *silver salt*,  $C_8H_{12}Ag_2O_4$ , prepared by the same method as that employed in the case of the *trans*-acid, gave the following result on analysis.

0.2210, on ignition, gave 0.1232 Ag.  $Ag = 55.74$ .

$C_8H_{12}O_4Ag_2$  requires  $Ag = 55.67$  per cent.

*Action of Heat on cis-Methylisopropylsuccinic acid.*—When gently boiled under reduced or ordinary pressure for a few minutes, or when slowly distilled, the acid readily loses water, and is converted into its own anhydride, and this, on boiling with water, again yields the *cis*-acid in a very pure condition. On treating a drop of this anhydride with a solution of sodium carbonate, on a watch glass, there is no evolution of carbon dioxide, so that the conversion is complete.

*The Anhydrides of cis- and trans-Methylisopropylsuccinic acids.*

*Anhydride of trans-Methylisopropylsuccinic acid.*—The simplest method of preparing this anhydride seemed to be the following. Five grams of the pure *trans*-acid were boiled with acetic anhydride for about two hours in a reflux apparatus, the solution poured into a glass dish, and the acetic anhydride evaporated as far as possible in a vacuum over potash. As no crystals separated after the lapse of five days, the product was distilled under reduced pressure (20 mm.), the anhydride passed over at 140–145° as a colourless oil, which, on standing, gradually solidified; it was pressed on a porous plate, and recrystallised from light petroleum (b. p. 80–100°), when it gave long, silky needles melting at 46°.

0.2010 gave 0.4520  $CO_2$  and 0.1534  $H_2O$ .  $C = 61.33$ ;  $H = 7.70$ .

$C_8H_{12}O_3$  requires  $C = 61.54$ ;  $H = 7.69$  per cent.

On boiling with water for half an hour, this anhydride dissolves, and, on cooling, the *trans*-acid separates in a very pure form, showing that the anhydride is in reality that of the *trans*-acid. The anhydride is not changed on distillation under reduced pressure, and even when rapidly distilled at the ordinary pressure it is only partially converted into the *cis*-modification. If, however, it be heated for a few minutes in a reflux apparatus and then distilled, it is converted



into the anhydride of the *cis*-acid, as shown by its yielding this acid on boiling with water, as also by its giving no precipitate with a benzene solution of aniline (see below).

*The Anhydride of cis-Methylisopropylsuccinic acid.*—This anhydride was prepared in the following manner. Five grams of the *cis*-acid were heated with acetic anhydride for two hours, and the solution placed over potash in a vacuum. As soon as the smell of acetic anhydride was no longer perceptible, the product was distilled under reduced pressure (25 mm.) when the anhydride passed over at 138—140° as a colourless oil; this, however, showed no signs of solidification, even when kept for a considerable time, and all subsequent efforts to procure it in a crystalline form proved fruitless. This anhydride, therefore, appears to be liquid at the ordinary temperature. An analysis of a sample which has been distilled under reduced pressure gave the following results.

0.1902 gave 0.4273  $\text{CO}_2$ , and 0.1333  $\text{H}_2\text{O}$ .  $\text{C} = 61.27$ ;  $\text{H} = 7.78$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.54$ ;  $\text{H} = 7.69$  per cent.

On boiling with water for half an hour, this anhydride dissolves, and on saturating the solution with hydrogen chloride, the *cis*-acid melting at 125—126° is obtained in a pure state.

*Conversion of the Anhydride of the trans-acid into that of the cis-acid.*

Three grams of the *trans*-anhydride were heated to boiling for three minutes under ordinary pressure in a flask shaped as shown in the figure, the flask being inclined, so that the liquid could constantly run back; the flask was then placed in a horizontal position, and the anhydride distilled into the receiver A under reduced pressure.



The liquid thus obtained showed no signs of solidification after prolonged standing, and, as it yielded the pure *cis*-acid on boiling with water, it is evident that a transformation of the *trans*- into the *cis*-modification had actually taken place under the conditions of the experiment.

*The Anilic acids and the Anil of cis- and trans-Methylisopropylsuccinic acids.*

(1) *The Action of Aniline on the trans-Anhydride.*—Two grams of this anhydride were dissolved in benzene, and a molecular proportion of

aniline, also dissolved in benzene, added; a thick, white precipitate separated immediately, the contents of the beaker becoming solid. The product was then collected, washed with benzene, dried, and recrystallised twice from dilute alcohol; the slender silky needles thus obtained melted at  $160^{\circ}$ , and decomposed at  $170^{\circ}$  with evolution of bubbles of steam. The substance dissolves readily in sodium carbonate solution.

A nitrogen determination of this compound and its behaviour on hydrolysis proved that it consisted of the anilic acid of *trans*-methylisopropylsuccinic acid of the formula 
$$\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\overset{(\text{CH}_3)_2\text{CH}\cdot\text{COOH}}{\underset{\text{CH}\cdot\text{CH}_3}{\text{C}}} \quad (?)$$

0.2590 gave 12.3 c.c. moist nitrogen at  $17^{\circ}$  and 753 mm.  $\text{N} = 5.45$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.62$  per cent.

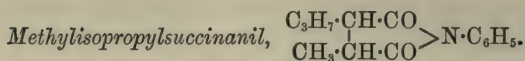
*Hydrolysis with Alcoholic Potash.*—About 1 gram of this anilic acid was heated with alcoholic potash for 12 hours on a water bath; on evaporating, acidifying, and extracting with ether, an acid was obtained which melted at  $160$ — $170^{\circ}$ , rising to  $174$ — $175^{\circ}$  after treatment with hot benzene. It consisted, therefore, of the *trans*-acid, the formation of which proves conclusively that the substance described above is in reality the *trans*-anilic acid.

(2) *The action of Aniline on the cis-Anhydride.*—On mixing a solution of 1 gram of the *cis*-anhydride dissolved in benzene with a benzene solution of a molecular proportion of aniline, no precipitate of the anilic acid was formed as in the case of the *trans*-anhydride, so that this difference in behaviour towards a benzene solution of aniline may be used as a ready means of identifying these anhydrides. On evaporating to dryness on the water bath, an oil was left which only solidified after standing two days in a vacuum, and repeatedly stirring; on grinding this up with cold benzene, filtering and washing with benzene, a white powder was left which crystallised from dilute alcohol in large, prismatic needles melting sharply at  $153^{\circ}$  and decomposing at  $160^{\circ}$ . Thinking that perhaps this might be the same substance as the anilic acid obtained from the *trans*-anhydride (m. p.  $160^{\circ}$ ), it was again recrystallised, but the melting point remained constant. A nitrogen estimation yielded the following figures.

0.2410 gave 11.9 c.c. moist nitrogen at  $16^{\circ}$  and 750 mm.  $\text{N} = 5.71$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.62$  per cent.

On hydrolysis with alcoholic potash, this substance yielded again the pure *cis*-acid, showing that it is in reality the anilide of the *cis*-acid.



The two anilic acids described above, when heated above their melting points, yield the same anil.

*The Anil obtained from the trans-Anilic acid.*—The *trans*-anilic acid was heated in a small test-tube in a sulphuric acid bath at  $200^\circ$ , until water ceased to be given off. On cooling, the anil remained as a thick, oily substance, which did not solidify on stirring, but it did so immediately on boiling with dilute ammonia. The insoluble matter was collected, washed with hot ammonia, and recrystallised from dilute alcohol, with the aid of animal charcoal. It is necessary to use a large quantity of the solvent, and to promote crystallisation by adding a crystal of the substance, otherwise owing to its low melting point and the higher temperature of the solvent, it frequently separates as an oil. This anilide crystallises in glistening plates melting at  $85^\circ$ ; it is insoluble in soda.

*The Anil obtained from the cis-Anilic acid.*—On heating this acid in the manner described, an anil was obtained, identical in melting point and crystalline form with that prepared from the *trans*-acid. A nitrogen estimation was made.

0.1136 gave 5.5 c.c. moist nitrogen at  $16^\circ$  and 759 mm.  $\text{N} = 5.74$ .

$\text{C}_{14}\text{H}_{17}\text{NO}_2$  requires  $\text{N} = 6.06$  per cent.

*Salts of cis- and trans-Methylisopropylsuccinic acids.*

In each case a 10 per cent. solution of the inorganic salt was added to a 10 per cent. solution of the ammonium salt of the acid.

	126° <i>cis</i> -	175° <i>trans</i> -
$\text{CuSO}_4$ .	<i>Cold</i> , no precipitate .....	The same.
"	<i>Hot</i> , no precipitate; but on cooling, the copper salt separates in flakes .....	"
$\text{Pb}(\text{NO}_3)_2$ .	<i>Cold</i> , white crystalline precipitate..	"
"	<i>Hot</i> , " "	"
$\text{Hg}_2(\text{NO}_3)_2$ .	<i>Cold</i> , white precipitate .....	"
"	<i>Hot</i> , soluble in excess .....	"
$\text{HgCl}_2$ .	<i>Cold</i> , no precipitate .....	"
"	<i>Hot</i> , " .....	White crystalline precipitate.
$\text{CaCl}_2$ .	<i>Cold</i> , no precipitate .....	"
"	<i>Hot</i> , " .....	"
$\text{Fe}_2\text{Cl}_6$ .	<i>Cold</i> , flocculent red-brown precipitate	"
"	<i>Hot</i> , " " "	"



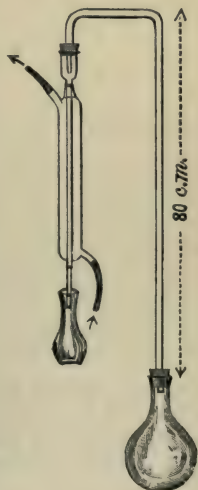
*The Action of Ethylic  $\alpha$ -Bromisovalerate on the Sodium Compound of Ethylic Methylmalonate in Alcoholic Solution.*

The action of ethylic  $\alpha$ -bromisovalerate on the sodium compound of ethylic methylmalonate was next investigated, in order to determine whether by this means the acids described above, or, perhaps, different ones, would be formed.

Six grams of sodium were dissolved in 60 grams of absolute alcohol, the solution mixed with 43 grams of ethylic methylmalonate, and 53 grams of ethylic  $\alpha$ -bromisovalerate added in small quantities at a time to the hot solution; a tolerably energetic action set in, and after three hours' heating on a water bath, the mass was found to be neutral. The alcohol was then distilled off, the product mixed with water, the oil which was deposited separated, and the aqueous liquid extracted six times with ether; after drying over calcium chloride, the ether was distilled off, and the residual oil fractionated under diminished pressure (67 mm.), when the chief fraction distilled between  $190^{\circ}$  and  $210^{\circ}$ ; the quantity was, however, only 10 grams, or not more than 15 per cent. of the theoretical yield.

*Hydrolysis of this Ethylic Salt.*—The ethereal salt was hydrolysed by boiling with a 50 per cent. solution of sulphuric acid in a round-bottomed flask, connected with Bischoff's reflux apparatus, and heated on a sand bath. As during the operation an acid oil distilled over with the alcohol, and collected in the receiver, a short Liebig's condenser was placed on the shorter arm of the apparatus, as shown in the figure, so as to ensure complete condensation, and from time to time the oil which had distilled was separated and returned to the flask. After three hours' boiling, all the oil had disappeared, and as, on adding water to the liquid, it dissolved without the separation of oily drops, the hydrolysis was considered as complete. The product was now distilled with steam, and, as in the previous experiment (p. 276), it was noticed that an oily substance distilled over first, and sank to the bottom of the receiver; at the end of two hours the oil ceased to come over, and as the distillate was only faintly acid, the distillation was stopped.

As no crystalline substance separated from the sulphuric acid solution on cooling, it was extracted with pure ether, and the ex-





tract, after drying, evaporated. The oil which was left did not solidify even when left in a vacuum over sulphuric acid for five days; it was therefore dissolved in water and the solution saturated with hydrogen chloride, but the substance was reprecipitated as an oil, no crystals being formed. The steam distillate, which contained, as stated above, an insoluble oil, was made strongly alkaline, evaporated to dryness on the water bath, mixed with excess of concentrated hydrochloric acid, and extracted with ether. The oily product, which solidified partially on standing, was dissolved in water and saturated with hydrogen chloride; the crystalline substance which separated melted at  $113-117^{\circ}$ , but after repeated recrystallisations it had a constant melting point of  $125-126^{\circ}$ .

An analysis gave the following figures.

0.2303 gave 0.4639  $\text{CO}_2$  and 0.1643  $\text{H}_2\text{O}$ .  $\text{C} = 54.94$ ;  $\text{H} = 7.93$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

The substance is therefore without doubt *cis*-methylisopropylsuccinic acid.

It is remarkable that in this reaction the *cis*-acid alone should be produced; no trace of the *trans*-acid could be isolated, and it could hardly have been overlooked, as it usually separates with great ease, and is readily purified.

*Action of Ethylic  $\alpha$ -Bromisovalerate on the Sodium Derivative of Ethylic Methylmalonate in Xylene Solution.*

As explained in the introduction, the object of this experiment was to determine whether, in xylene solution, the condensation between ethylic bromovalerate and ethylic methylmalonate might not proceed in a different manner from that in alcoholic solution, yielding derivatives of glutaric acid.

Fifteen grams of sodium in the form of powder\* (molecular sodium) were suspended in about 400 c.c. of xylene and 117 grams of ethylic methylmalonate added; at the ordinary temperature the sodium dissolved only slowly, but, on slightly warming, a violent evolution of hydrogen took place, and the sodium derivative of ethylic methylmalonate separated as a pasty mass, in fact, the contents of the flask became so thick that more xylene had to be added. Ethylic  $\alpha$ -bromisovalerate (141 grams) was then poured into the cooled solution, but no perceptible action occurred, although the sodium derivative dissolved in the mixture; the flask was therefore connected with a reflux condenser and heated to boiling on a sand bath for five hours, when sodium bromide separated in large quantities.

\* As obtained by melting the sodium under the xylene in a corked flask and shaking vigorously.

When cold, the product was mixed with water, the xylene solution separated, and the aqueous liquid extracted three times with small quantities of xylene. The combined extracts were dried with calcium chloride, and the xylene distilled off as far as possible under the ordinary pressure; as soon, however, as the thermometer began to rise rapidly, the residue was transferred to a smaller flask, and the fractionation continued under diminished pressure (80 mm.); the chief fraction distilled at 200—210°, and weighed 71 grams, or 35 per cent. of the theoretical yield of pure ethylic salt.

*Hydrolysis of the Ethylic Salt.*—This ethereal salt was hydrolysed by means of a 50 per cent. solution of sulphuric acid in the manner described in the previous instance (p. 284); after 12 hours, all oil having disappeared, the product was distilled with steam.

The *sulphuric acid solution*, on cooling, deposited a large quantity of crystals, which melted indefinitely at 160—170°, but on twice recrystallising from water, the melting point rose to 174—175°, and remained constant. The following figures were obtained on analysis, showing that the substance was *trans-methylisopropylsuccinic acid*.

0.2102 gave 0.4327 CO<sub>2</sub> and 0.1512 H<sub>2</sub>O. C = 54.97; H = 7.99.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17; H = 8.04 per cent.

The filtrate from these crystals, on extraction with ether, &c., gave an oily residue, which, on standing, partially solidified; it was then spread on a porous plate, and the solid residue recrystallised from concentrated hydrochloric acid, when an acid was obtained melting sharply at 115—116°. This was evidently isopropylsuccinic acid,\* since, on analysis, it yielded the following result.

0.2403 gave 0.4657 CO<sub>2</sub> and 0.1667 H<sub>2</sub>O. C = 53.07; H = 7.70.

C<sub>7</sub>H<sub>12</sub>O<sub>4</sub> requires C = 52.52; H = 7.52 per cent.

*The Steam Distillate.*—As in the previous experiment (p. 285) this was made strongly alkaline with potash, evaporated to dryness, concentrated hydrochloric acid then added in large excess, and the whole extracted with ether; in this way, a solid substance was obtained which melted roughly at 110—120°, and on recrystallising four times from concentrated hydrochloric acid, gave *cis-methylisopropylsuccinic acid* melting constantly at 125—126°.

0.1926 gave 0.3905 CO<sub>2</sub> and 0.1388 H<sub>2</sub>O. C = 55.29; H = 8.01.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17; H = 8.04 per cent.

The quantities of these two acids melting at 126° and 175° respectively were about equal.

\* The formation of this substance is obviously due to the presence of traces of ethylic malonate in the ethylic methylmalonate used.

*Cis*- and *trans*-methylisopropylsuccinic acids are therefore formed in about equal proportion by the action of ethylic  $\alpha$ -bromisovalerate on the sodium compound of ethylic methylmalonate in xylene solution, whereas the same condensation conducted in alcoholic solution yields the *cis*-modification only.

# SUBSTITUTED PIMELIC ACIDS.

BY

A. W. CROSSLEY, B.Sc., PH.D.,

AND

W. H. PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1894.]

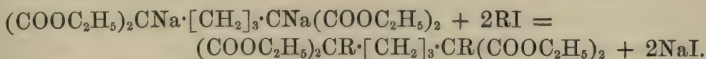




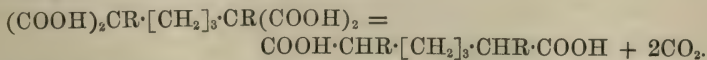
### Substituted pimelic acids.

By A. W. CROSSLEY, B.Sc., Ph.D., Berkeley Fellow of the Owens College, and W. H. PERKIN, Jun.

SOME time since (Trans., 1891, **59**, 818) one of us, in conjunction with Mr. Bertram Prentice, described a method of preparing  $\alpha\alpha_1$ -disubstituted pimelic acids, which, briefly stated, is as follows. The disodium derivative of ethylic pentanetetracarboxylate is digested with the iodide of a radicle (RI), and thus converted into a di-derivative of this ethereal salt.



On hydrolysis, this salt yields the corresponding tetrabasic acid, which, when heated at about  $200^\circ$ , loses 2 mols. of carbon dioxide, forming an  $\alpha\alpha_1$ -disubstituted-pimelic acid.

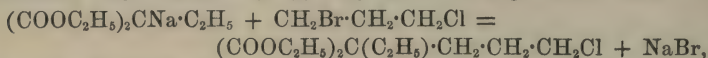


With the object of preparing mono-substituted pimelic acids, experiments were made on the action of alkyl haloids on ethylic pentanetetracarboxylate in the presence of only 1 mol. of sodium

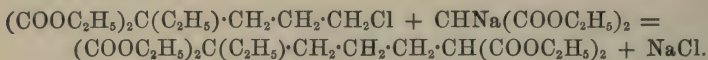
ethylate; but these were not successful, as, in such cases, half of the ethylic pentanetetracarboxylate remained unacted on, the other half having been converted into a disubstitution product (*loc. cit.*, p. 819).

In continuing the study of this subject, various modifications of the above synthetical method were tried, in the hope of discovering some means by which not only mono-substituted pimelic acids, but also  $\alpha\alpha_1$ -disubstituted pimelic acids, containing two different radicles of the type  $\text{COOH}\cdot\text{CHR}\cdot[\text{CH}_2]_3\cdot\text{CHR}'\cdot\text{COOH}$ , might be prepared; this was ultimately accomplished in several ways.

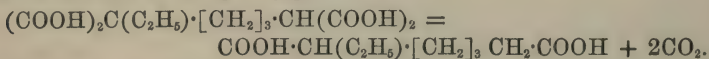
When trimethylene chlorobromide (*ww*<sub>1</sub>-chlorobromopropane,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ ) acts on the sodium derivative of ethylic ethylmalonate, ethylic *w*-chloropropylethyl malonate is produced, thus.



and this substance, when digested in alcoholic solution with the sodium derivative of ethylic malonate, yields ethylic ethylpentanetetracarboxylate,



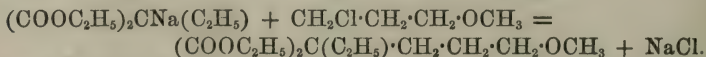
On hydrolysis, this ethereal salt yields an acid, which at  $200^\circ$  loses carbon dioxide, forming ethylpimelic acid.



The new acid was purified by first converting it into its ethylic salt, and then, after fractionation, reconverting this into the acid by hydrolysis; the oily product was subsequently distilled under reduced pressure, when it boiled constantly at  $260\text{--}265^\circ$  (82 mm.), but did not solidify, even after many weeks; it gave a crystalline *dianilide*,  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$  (m. p.  $145^\circ$ ), however, which, although not a very characteristic compound, might possibly serve for the identification of the acid.

The next acid which was prepared was ethylmethylpimelic acid,  $\text{COOH}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ . The method used in synthesising it, and which worked very well, differs in some respects from that described above, and is briefly as follows.

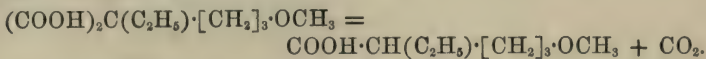
In the first place, the sodium derivative of ethylic ethylmalonate was digested in alcoholic solution with chloromethoxypropane (Trans., 1894, 65, 596), when the following interaction took place.



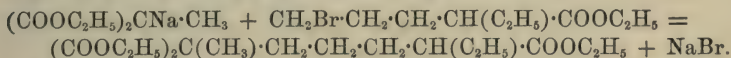
The methylic\* methoxypropylethylmalonate obtained was con-

\* By mistake, methylic alcohol was used as the solvent instead of ethylic alcohol

verted into the corresponding acid by hydrolysis; this, on distillation, is decomposed, evolving carbon dioxide and forming methoxypropylethylacetic acid.



On treatment with hydrobromic acid, this methoxy-acid yields bromopropylethylacetic acid, the ethereal salt of which readily interacts with the sodium derivative of ethylic methylmalonate, yielding ethylic ethylmethylpentanetricarboxylate, thus.



Lastly, this ethereal salt, on hydrolysis, is converted into the corresponding tricarboxylic acid, from which, by heating at  $200^\circ$  and subsequent distillation, ethylmethylpimelic acid,



is obtained in the usual manner.

This acid boiled constantly at  $265\text{--}270^\circ$ , under a pressure of 80 mm. It remained as an oil during several weeks, but was put aside, and at the end of about four months was found to have deposited crystals; these, after repeated recrystallisation, melted at  $78^\circ$ .

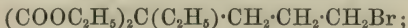
It seems probable that this acid exists in two stereoisomeric forms; this would account for the extreme slowness with which the oily acid crystallises, and also for the great difficulty experienced in purifying it by recrystallisation; we propose to further investigate this subject, and also to prepare several other substituted pimelic acids, some of which it is expected will have interesting properties.



The first experiments made with the object of preparing this acid were carried out as follows.

Sodium (2.3 grams) was dissolved in absolute alcohol (25 grams), the well-cooled solution mixed with carefully purified ethylic ethylmalonate (18.8 grams) and trimethylene bromide (21 grams), and the whole heated in a reflux apparatus for one hour, when the mixture was found to be neutral.

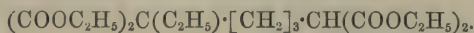
The product contains a bromo-derivative, which was not analysed, but obviously consists of ethylic bromopropylethylmalonate,



this was mixed with sodium (2.7 grams), previously dissolved in ab- in these experiments. The product, therefore, consisted of the methylic salt, an interchange of an alkyl radicle having taken place (compare Purdie and Marshall, *Trans.*, 1888, 53, 391).



solute alcohol (25 grams), ethylic malonate (16 grams) added, and the mixture heated in a reflux apparatus for three hours, when it was found to be almost neutral. Water was now added, and the precipitated oil extracted by agitating thrice with ether; the ethereal solution was then washed with water, dried over calcium chloride, the ether distilled off, and the residual light yellow oil submitted to careful fractionation under reduced pressure. In this way, a colourless oil was obtained, boiling constantly at  $275^{\circ}$  under a pressure of 75 mm., and giving, on analysis, numbers agreeing with those required for ethylic ethylpentanetetracarboxylate,



	Found.	Theory. $\text{C}_{19}\text{H}_{32}\text{O}_8$ .
C .....	58.73 per cent.	58.76 per cent.
H .....	8.46     ,,	8.24     ,,

This oil was hydrolysed by boiling with excess of alcoholic potash for three hours; the alkaline product was then diluted with water, evaporated till free from alcohol, acidified, and extracted ten times with ether. On drying over calcium chloride, and evaporating the ether, a thick, colourless oil was left; this was heated at  $200^{\circ}$  until no further evolution of carbon dioxide took place, and then rapidly distilled under reduced pressure; nearly the whole passed over between  $250^{\circ}$  and  $260^{\circ}$  (70 mm.), and, on analysis, gave the following results.

	Found.	Theory. $\text{C}_9\text{H}_{16}\text{O}_4$ .
C .....	57.82 per cent.	57.44 per cent.
H .....	8.75     ,,	8.51     ,,

These numbers agree fairly well with those required for ethylpimelic acid,  $\text{COOH}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot[\text{CH}_2]_3\cdot\text{CH}_2\cdot\text{COOH}$ , and judging from the results of subsequent experiments, there can be no doubt that it consisted of this acid in a nearly pure state.

As this acid, even after long standing, showed no signs of crystallising (which is remarkable in consideration of the fact that pimelic acid and all its alkyl-derivatives which have hitherto been prepared, are solids), it was assumed that this behaviour was due to impurity, a supposition borne out by the above analyses, the rather high values for carbon and hydrogen found indicating the presence of traces of diethylpimelic acid,  $\text{COOH}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot\text{COOH}$ .

The preparation of the acid was therefore modified in the following way.

Sodium (3.6 grams), dissolved in alcohol (50 grams), was mixed with ethylic ethylmalonate (29 grams) and trimethylene chlorobromide (24 grams), and heated as before until neutral. Water was then added, the oily product of the reaction extracted with ether, the

etheral solution well washed with water, dried over calcium chloride, evaporated, and the residual oil allowed to remain for some days over sulphuric acid in a vacuum.

The analyses of this preparation gave the following results, which agree only approximately with those for ethylic chloropropylethylmalonate  $(\text{COOC}_2\text{H}_5)_2\text{C}(\text{C}_2\text{H}_5)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ .

	Found.		Theory.
	I.	II.	$\text{C}_{12}\text{H}_{21}\text{O}_4\text{Cl}$ .
Cl .....	11.43	11.52 per cent.	13.42 per cent.

This oily substance was then digested with sodium ethoxide (3.6 grams sodium dissolved in 50 grams of alcohol) and ethylic malonate (24 grams) until the product was quite neutral; water was added, the oily ethereal salt extracted as before, and purified by fractional distillation under reduced pressure. The greater part distilled at  $270\text{--}275^\circ$  (75 mm. pressure), and consisted of ethylic ethylpentanetetetracarboxylate.

This was hydrolysed with alcoholic potash as before, and the resulting crude ethylpimelic acid, which, again, did not crystallise, purified by conversion into its ethylic salt in the following way.

The crude acid was dissolved in about five times its bulk of absolute ethylic alcohol, mixed gradually with one-third of its volume of concentrated sulphuric acid, and the mixture allowed to stand for 48 hours; at the end of this time it was diluted with water, the oily ethereal salt extracted with ether, the ethereal solution washed with dilute sodium carbonate solution, dried over potassium carbonate, evaporated, and the brownish, oily residue purified by fractionation under reduced pressure.

*Ethylic ethylpimelate*,  $\text{COOC}_2\text{H}_5\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot[\text{CH}_2]_4\cdot\text{COOC}_2\text{H}_5$ , is a colourless, oily liquid, possessing a faint smell, and boiling at  $198\text{--}200^\circ$  under a pressure of 83 mm.

	Found.	Theory. $\text{C}_{13}\text{H}_{24}\text{O}_4$ .
C .....	64.17 per cent.	63.93 per cent.
H .....	10.27 „	9.83 „

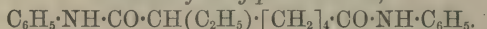
This ethylic salt was hydrolysed by boiling with alcoholic potash, and the ethylpimelic acid formed was extracted with ether, dried with calcium chloride, and fractionated; almost the whole passed over as a colourless oil between  $260^\circ$  and  $265^\circ$  under a pressure of 82 mm. It gave the following results on analysis.

	Found.	Theory. $\text{C}_9\text{H}_{16}\text{O}_4$ .
C .....	57.76 per cent.	57.44 per cent.
H .....	8.73 „	8.51 „

In this case, also, the acid could not be made to crystallise, so that

we must conclude either that ethylpimelic acid is an oil, or, that when prepared by the above methods, small quantities of impurities are present which prevent it from crystallising.

*Anilide of ethylpimelic acid,*



In order, if possible, to obtain a crystalline anilide of this acid, by means of which the acid might be identified, a portion of the substance was digested for 20 hours in a reflux apparatus with about four times its volume of pure aniline. The dark coloured product was dissolved in ether, the ethereal solution well washed with dilute hydrochloric acid to remove excess of aniline, dried over calcium chloride and evaporated; the thick, oily residue, after standing over sulphuric acid in a vacuum for a time, partially solidified. This crude substance, after being washed with ether and crystallised several times from benzene, was obtained as a colourless, indistinctly crystalline powder, melting at  $145^\circ$ ; on analysis it gave the following numbers.

	Found.	Theory. $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$ .
C .....	74.39 per cent.	74.55 per cent.
H ....	8.10 „	7.69 „
N .....	8.29 „	8.25 „

It is readily soluble in hot benzene, alcohol, and chloroform, but only sparingly in light petroleum.

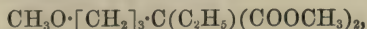
*Ethylmethylpimelic acid*,  $\text{COOH}\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$ .

The method employed in the synthesis of this disubstituted pimelic acid, containing two different radicles, was somewhat different from that used for ethylpimelic acid, and is probably applicable in the case of all similarly constituted acids.

Sodium (2.3 grams) was dissolved in absolute methylic alcohol (30 grams), ethylic ethylmalonate (18.8 grams) added, and then chloromethoxypropane (10.8 grams), when a vigorous action set in; as soon as this had subsided, the mixture was heated in a reflux apparatus for about an hour and a half, and after diluting with water, extracting with ether, &c., as in the case of ethylic ethylpentanetetra-carboxylate (p. 990), was submitted to fractionation under reduced pressure, when the greater part distilled at  $180^\circ$  (43 mm.). On analysis it gave the following results.

	Found.		Theory.	
	I.	II.	$\text{C}_{11}\text{H}_{20}\text{O}_5$ .	$\text{C}_{13}\text{H}_{24}\text{O}_5$ .
C ....	55.17	55.97 per cent.	56.89	59.77 per cent.
H ....	8.34	8.64 „	8.62	9.23 „

These numbers agree best with the formula  $C_{11}H_{20}O_5$ , that of methylic methoxypropylethylmalonate,



the formation of which is explained in the introduction, the slight deficiency in carbon and hydrogen being due to the fact that the oil contains traces of chlorine.

This methylic salt yielded the acid on hydrolysis, which was purified by fractionation under ordinary pressure. The whole passed over between  $240$  and  $255^\circ$ , and a portion boiling at  $250^\circ$  gave the following results on analysis.

	Found.	Theory. $C_8H_{16}O_3$ .
C .....	59.82 per cent.	60.00 per cent.
H .....	10.47 „	10.00 „

*Methoxypropylethylacetic acid*,  $COOH \cdot CH(C_2H_5) \cdot [CH_2]_3 \cdot OCH_3$ , is a thick, colourless oil, which did not solidify after standing for two days; when heated with hydrobromic acid it is readily converted into *bromopropylethylacetic acid*,  $COOH \cdot CH(C_2H_5) \cdot CH_2 \cdot CH_2 \cdot CH_2Br$ .

In order to prepare this substance the methoxy-acid was dissolved in twice its volume of fuming hydrobromic acid, and the solution heated in a sealed tube at  $150^\circ$  for two hours. On cooling, it was observed that two distinct layers had formed, and on pouring the product into water a heavy oil was deposited; this was extracted by agitation with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated. The dark brown, oily acid thus obtained did not solidify, and as it could not be purified by fractional distillation, was directly submitted to analysis. The numbers obtained agree only approximately with those required for bromopropylethylacetic acid.

	Found.	Theory. $C_7H_{13}O_2Br$ .
Br .....	35.27 per cent.	38.27 per cent.

The acid was converted into the ethylic salt by dissolving it in ethylic alcohol, saturating the solution with hydrogen chloride, and, after 24 hours, pouring the product into water; the oily layer was extracted with ether, and the ethereal solution washed with sodium carbonate solution, dried over calcium chloride, and evaporated.

In order to obtain ethylic ethylmethylpentanetricarboxylate,  $COOC_2H_5 \cdot CH(C_2H_5) \cdot [CH_2]_3 \cdot C(CH_3)(COOC_2H_5)_2$ , the sodium compound of ethylic methylmalonate was prepared by adding ethylic methylmalonate (17 grams) to a solution of sodium (2 grams) in ethylic alcohol (25 grams), ethylic bromopropylethylacetate (20 grams) was then added, and the mixture heated for  $2\frac{1}{2}$  hours in a reflux apparatus. On adding water, extracting with ether &c., in the usual manner, and purifying the product by fractionation under



reduced pressure, almost the whole distilled at 227—230° (60 mm. pressure). It gave the following results on analysis.

	Found.		Theory. $C_{17}H_{30}O_6$ .
	I.	II.	
C .....	62.05	61.92 per cent.	61.81 per cent.
H .....	9.86	9.31 „	9.09 „

The fraction of this substance boiling at 227—230° (60 mm.) was then hydrolysed by boiling with alcoholic potash, and the free acid obtained by extracting with ether, &c., in the usual manner. On heating it at 200° until no further evolution of carbon dioxide was noticeable, and purifying the residual dark brown, oily acid by distillation under reduced pressure almost the whole passed over at 265—270° (80 mm.). It gave the following results on analysis.

	Found.	COOH·CH(CH <sub>3</sub> )·[CH <sub>2</sub> ] <sub>3</sub> ·CH(C <sub>2</sub> H <sub>5</sub> )·COOH.	Theory.
C .....	59.28 per cent.		59.40 per cent.
H .....	9.43 „		8.91 „

These numbers agree well with those required for ethylmethylpimelic acid, and the formula of the acid was further corroborated by preparing and analysing the silver salt.

A small quantity of the acid was neutralised with ammonia solution, and a few drops of dilute silver nitrate added; after filtration from the slight precipitate, the clear liquid was heated to boiling and precipitated by adding a large excess of silver nitrate. The white, insoluble silver salt was collected, well washed with water, and analysed with the following results.

	Found.		Theory. $C_{10}H_{16}O_4Ag_2$ .
	I.	II.	
Ag .....	51.68	51.72 per cent.	51.92 per cent.

The acid remained liquid for a long time, but after standing for four months it gradually deposited crystals, and became semi-solid; the oil was gradually absorbed when the crystals were left in contact with porous porcelain, leaving a mass of almost colourless crystals, which melted approximately at 58°.

By repeated recrystallisation from water, with the aid of animal charcoal, the crude product yielded a magnificent crystalline acid, which melted at 78° and gave the following results on analysis.

	Found.	Theory. $C_{10}H_{18}O_4$ .
C .....	59.51 per cent.	59.45 per cent.
H .....	9.10 „	8.91 „

Ethylmethylpimelic acid crystallises from water in large, transparent, glistening prisms; it is sparingly soluble in cold water, and

is deposited from the hot, concentrated aqueous solution, on cooling, as an oil, which crystallises rapidly if stirred with a glass rod.

The aqueous mother-liquors of the acid, on concentration, yield different fractions of crystalline acids, which melt roughly between  $60^{\circ}$  and  $75^{\circ}$ , and presumably contain a second isomeride of ethyl-methylpimelic acid. Owing, however, to the very small quantity of material at our disposal, this second acid, if present, could not be isolated, and for this reason we could not recrystallise the ethyl-pimelic acid (m. p.  $78^{\circ}$ ) as often as we could have wished, and give, therefore, the melting-point of this acid only as a close approximation.

*Chemical Laboratory,  
Owens College, Manchester.*



# NOTE ON THE PREPARATION OF GLYCOL.

BY

EDWARD HAWORTH, B.Sc.,

AND

WILLIAM HENRY PERKIN, JUN.

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[From the Transactions of the Chemical Society, 1896.]





### Note on the preparation of glycol.

By EDWARD HAWORTH, B.Sc., and WILLIAM HENRY PERKIN, Jun.

IN preparing glycol by the usual method, namely, digesting ethylene dibromide with potassium carbonate solution, evaporating the product nearly to dryness, and extracting the glycol by means of a mixture of ether and alcohol, a very small yield only is obtained, due principally to the volatility of the glycol with steam, and consequent loss during the evaporation.

As we required a considerable quantity of glycol for some synthetical work, we made many experiments with the object of

improving the method of preparation, and found that by the following simple modifications of the usual process, the yield may be greatly increased.

In the first place, potassium carbonate (138 grams) is dissolved in water (1 litre), and the solution boiled in a stout, round-bottomed flask with ethylene dibromide (188 grams) in a reflux apparatus, from the top of which a glass tube leads to a couple of wash bottles containing bromine. When almost all the oily drops have disappeared (which is usually the case after 8—10 hours), the same quantities of potassium carbonate and ethylene dibromide are again added to the solution, and the boiling continued as before; the operation being repeated until 1128 grams of ethylene dibromide have been decomposed.

After the third addition of ethylene dibromide, crystals of potassium bromide separate on standing over night. These (and those which separate after each succeeding operation) are removed in the morning, by filtration on a vacuum pump, before the action is again started. The crystals are then washed with absolute methylated spirit, the washings being subsequently used for the isolation of the glycol, as explained below. After the decomposition of the ethylene dibromide is complete, the solution of glycol is heated in an oil bath to slowly distil off the water, using a colonna to prevent, as far as possible, loss of glycol by evaporation.

When the distillation has continued some time, the liquid begins to bump violently, owing to the separation of potassium bromide. The solution is now cooled, the crystals of potassium bromide removed, as before, and the distillation then continued. All the water which distils over should be carefully preserved for use in a subsequent preparation. When the solution becomes very viscid, and the temperature of the vapour passing over begins to rise, the distillation is stopped, and the residue is mixed with the methylated spirit employed in washing the potassium bromide crystals, as explained above. After standing for some time, the crystals of potassium bromide, which separate in quantity, are removed by filtration on the pump, washed with absolute methylated spirit, and the combined alcoholic extracts concentrated by slow distillation, as before, from a flask fitted with a colonna.

The residue is then again treated with absolute methylated spirit, which separates more potassium bromide; this treatment is repeated, now using a mixture of alcohol and ether, until almost the whole of the potassium bromide has been removed.

The solvent is then removed by distillation, and the residual glycol fractionated, first under reduced pressure, and finally at the ordinary pressure.

The yield of glycol obtained in this way is about 50—60 per cent. of the theoretical, and we have found it practicable in one apparatus to prepare 1 kilo. of glycol in about 10—14 days.

During the action, considerable quantities of vinylic bromide are formed; this is absorbed by the bromine in the wash bottles, and by subsequently treating the product with dilute potash, to remove the excess of bromine, and fractionation, tribromethylene,  $\text{CH}_2\text{Br}\cdot\text{CHBr}_2$ , is readily obtained in a pure state.

*Owens College,  
Manchester.*





NOTE ON  $\gamma$ -ACETOBUTYRIC ACID,  
 $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .

BY

W. H. BENTLEY

AND

W. H. PERKIN, JUN.

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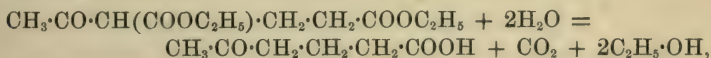
[From the Transactions of the Chemical Society, 1896.]



**Note on  $\gamma$ -Acetobutyric acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .**

By W. H. BENTLEY and W. H. PERKIN, jun.

DURING the course of an investigation on sulphocamphylic acid, the results of which, it is hoped, will soon be ready for publication, a ketonic acid was obtained, which had many properties in common with, and was for a long time thought to be,  $\gamma$ -acetobutyric acid. This acid has already been prepared by Wolff (*Annalen*, 1883, **216**, 129) from ethylic acetylglutarate, by hydrolysis with dilute hydrochloric acid,



and by Lipp (*Ber.*, 1885, **18**, 3251), by the oxidation of acetobutylic alcohol,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , with potassium dichromate and sulphuric acid.

It is a colourless oil, which boils at  $274\text{--}275^\circ$  with slight decomposition; it solidifies in a freezing mixture with difficulty, the crystalline substance melting at  $13^\circ$ , whilst with water it yields a crystalline hydrate,  $\text{CH}_3\cdot\text{C}(\text{OH})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , which melts at  $35\text{--}36^\circ$ . As these properties of acetobutyric acid proved to be altogether insufficient for the purposes of comparison with the acid obtained from sulphocamphylic acid, we have prepared considerable quantities of the former and carefully examined two new derivatives,



namely, the *oxime*,  $\text{CH}_3\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$  (m. p. 104—105°), and the *semicarbazone*,  $\text{CH}_3\cdot\text{C}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH} \\ \text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \end{smallmatrix}$  (m. p. 173—174°), which are well characterised, and will serve in future for the identification of the acid.

At the same time, we have introduced some improvements into the preparation of this acid, and hope that the following short account will be of value to subsequent investigators.

*Preparation of  $\gamma$ -Acetobutyric acid*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .

The method which we employed in the preparation of this acid was similar to that recommended by Wolff and mentioned above, namely, by the hydrolysis of ethylic acetoglutarate. Sodium (3·4 grams) is dissolved in alcohol (45 grams), and to the well-cooled solution, first ethylic acetoacetate (19 grams) and then ethylic  $\beta$ -iodopropionate (33 grams) are added. The reaction takes place readily, the mixture getting quite hot; after standing for half an hour, the whole is heated on a water bath for two hours, water is then added, and the oily product extracted with ether. The ethereal solution after being well washed with water containing a little sulphurous acid to remove traces of iodine, is dried over calcium chloride, evaporated, and the oily residue, which weighs about 26 grams, is purified by distillation under reduced pressure (50 mm.). The crude substance commences to boil at 130°, but, after a few drops have passed over, the temperature rises rapidly to 190°, and nearly the whole passes over between this and 200°, a small quantity only of a residue of high boiling point remaining in the retort. Pure ethylic acetylglutarate is a colourless oil, which boils at 195—197° (50 mm.); on analysis, it gave the following result.

0·1180 gave 0·2478  $\text{CO}_2$  and 0·0845  $\text{H}_2\text{O}$ .  $\text{C} = 57\cdot27$ ;  $\text{H} = 7\cdot94$ .

$\text{C}_{11}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 57\cdot39$ ;  $\text{H} = 7\cdot83$  per cent.

It is best to distil this ethereal salt under reduced pressure, as it is then readily obtained pure, whereas, if distilled at the ordinary pressure, as recommended by Wislicenus and Limpach, it decomposes somewhat, owing to the high temperature at which it boils (271—272°).

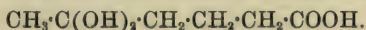
In order to obtain acetobutyric acid, the fraction of the ethereal salt distilling at 190—200° (50 mm.) is boiled in a reflux apparatus with 5 vols. of dilute hydrochloric acid (1 vol. of concentrated acid to 2 vols. of water). The oily layer rapidly disappears with evolution of carbon dioxide, and hydrolysis is complete after five hours, although Wolff recommends boiling for 8—10 hours. In order to isolate the product, Wolff fractionated the hydrochloric acid liquid direct, but this always causes considerable decomposition of the acetobutyric acid,

and we found that a much better result was obtained by proceeding as follows. The acid liquid, while still warm, is saturated with ammonium sulphate, and the acetobutyric acid, nearly the whole of which separates on the surface as an oily liquid, is extracted six times with ether. The ethereal solution is dried over calcium chloride, evaporated, and the residual, almost colourless oil is fractionated under reduced pressure, when almost the whole distils at  $195-200^{\circ}$  (65 mm.), the yield being about 85 per cent. of the theoretical.

0.1322 gave 0.2676  $\text{CO}_2$  and 0.0926  $\text{H}_2\text{O}$ .  $\text{C} = 55.20$ ;  $\text{H} = 7.79$ .

$\text{C}_6\text{H}_{10}\text{O}_3$  requires  $\text{C} = 55.38$ ;  $\text{H} = 7.69$  per cent.

The acetobutyric acid prepared in this way was a perfectly colourless, moderately thick oil, which when mixed with a little water rapidly solidified to colourless crystals of the hydrate



*Oxidation with Nitric acid.*—A few grams of the pure acid were gently heated with nitric acid (sp. gr. 1.2) in a reflux apparatus, when oxidation soon commenced, red fumes being copiously evolved. After boiling for about two hours, the product was diluted with water, evaporated to dryness on the water bath, and the crystalline residue, after being left in contact with porous porcelain until colourless, was recrystallised from concentrated hydrochloric acid. The colourless crystals which separated melted at  $180-183^{\circ}$ , and were found to consist of pure *succinic acid*, the oxidation having taken place at the  $\gamma\text{-CH}_2$  group marked \*,



It was at first thought probable that the reaction might take place in such a way that glutaric acid would be produced; probably this acid is formed when bromine in presence of potash is used as the oxidising agent, as in this case quantities of tetrabromomethane,  $\text{CBr}_4$ , are deposited in a crystalline condition.

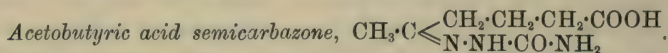
*Oxime of Acetobutyric acid*,  $\text{CH}_3\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ .

This was prepared by dissolving hydroxylamine hydrochloride (5 grams) in a small quantity of water, adding acetobutyric acid (6 grams) and then, after cooling, mixing the clear solution with a concentrated solution of potash (7 grams). After 20 hours, the liquid was acidified, saturated with ammonium sulphate, and extracted at least 25 times with ether. The ethereal solution was dried over calcium chloride, evaporated, and the solid residue purified by recrystallisation from benzene.

0.1563 gave 13 c.c. moist nitrogen at  $18^{\circ}$  and 760 mm.  $\text{N} = 9.60$ .

$\text{C}_6\text{H}_{11}\text{NO}_3$  requires  $\text{N} = 9.65$  per cent.

The *oxime* of *acetobutyric acid* crystallises from benzene in colourless prisms, and melts at 104—105°. It is readily soluble in alcohol, water, and hot benzene, but only sparingly in ether, light petroleum, or cold benzene.



In order to prepare this substance, semicarbazide hydrochloride was dissolved in a very little warm water, the solution mixed with an equal quantity of hot concentrated sodium acetate solution, the acetobutyric acid added, and the clear liquid heated to boiling for a few seconds; on cooling, the semicarbazone rapidly separated in crystals, which, after standing over night, were collected, washed, and purified by recrystallisation from a little hot water.

0.1016 gave 20 c.c moist nitrogen at 19° and 758 mm.  $\text{N} = 22.56$ .

$\text{C}_7\text{H}_{13}\text{N}_3\text{O}_3$  requires  $\text{N} = 22.46$  per cent.

*Acetobutyric acid semicarbazone*, when heated in a capillary tube, softens at 168°, and melts and decomposes at 173—174°. It is readily soluble in hot water, and crystallises from the solution on cooling in colourless, glistening needles.

THE REDUCTION OF XYLIC ACID, OF PARAXYLIC  
ACID AND OF METHYLTEREPHTHALIC ACID,  
AND THE PREPARATION OF METHYLTEREPHTHALIC  
ACID AND OF METHYLISOPHTHALIC  
ACID.

BY

WILLIAM HENRY BENTLEY

AND

WILLIAM HENRY PERKIN, JUN.

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From the Transactions of the Chemical Society, 1897.





The reduction of Xylic Acid, of Paraxylic Acid and of Methylterephthalic Acid, and the preparation of Methylterephthalic Acid and of Methylisophthalic Acid.

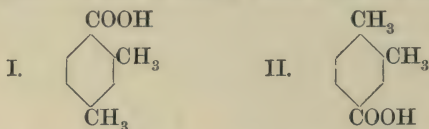
By WILLIAM HENRY BENTLEY and WILLIAM HENRY PERKIN, Jun.

KACHLER (*Annalen*, 1873, 169, 183) first showed that sulphocamphylic acid,  $C_9H_{14}SO_5$ , is decomposed when fused with potash with formation of a monobasic acid,  $C_9H_{12}O_2$ , melting at  $148^\circ$ .

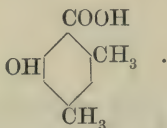


and subsequently Damsky (*Ber.*, 1887, 20, 2965) obtained, by the same reaction, a second acid of this formula melting at  $99^{\circ}$ . This action of fused soda or potash on sulphocamphylic acid has been made the subject of an extended investigation by one of us (compare Proceedings, 1893, 109; 1895, 23; 1896, 189), in the hope of discovering the constitution of the two isomeric acids  $C_9H_{12}O_2$ , and of thus obtaining evidence as to the constitution of sulphocamphylic acid and, indirectly, also, of that of camphoric acid itself.

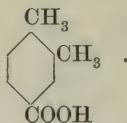
During the course of the examination of these two acids, which were named  $\alpha$ -camphylic acid (m. p.  $148^{\circ}$ ) and  $\beta$ -camphylic acid (m. p. about  $104^{\circ}$ ), some facts came to light which seemed to point to the conclusion that these substances might be closely allied to *xylic acid*, I, or *paraxylic*



*acid*, II, and this seemed all the more probable when it was remembered that sulphocamphylic acid itself could be converted into derivatives of these acids by two widely different processes. When sulphocamphylic acid is oxidised with potassium permanganate (*Proc.*, 1893, 109), it yields a dibasic acid of the formula  $C_{18}H_{22}O_7$ , which, by the action of concentrated sulphuric acid, is converted into a hydroxyxylic acid of the probable constitution



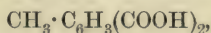
Again, Koenigs and Meyer (*Ber.*, 1894, 27, 3465) found that when *isolauronic acid*,  $C_9H_{14}O_2$ , which is formed by the action of heat on sulphocamphylic acid ( $C_9H_{14}SO_5, H_2O = C_9H_{14}O_2 + H_2SO_4$ ) is oxidised with permanganate it yields isolauronic acid,  $C_9H_{12}O_3$ , and that the latter acid, when warmed on the water bath with sulphuric acid, is converted into paraxylic acid,



As these xylic and paraxylic acids may be obtained in this way from sulphocamphylic acid, it seemed possible that the two camphylic acids,  $C_9H_{12}O_2$ , might be dihydro-derivatives of these acids and that the acids,

$C_9H_{14}O_2$ , which may be obtained from them by reduction with sodium amalgam, were the corresponding tetrahydro-acids. In order to determine whether this view was correct, we decided to investigate the action of reducing agents on the xylic acids, and beg to lay an account of the results of our experiments before the Society.

The xylic and paraxylic acids required for this research were first prepared by the method described by Fittig and Laubinger (*Annalen*, 1869, 151, 269), which consists in oxidising pseudocumene by means of dilute nitric acid. The product of this reaction contains, besides the two xylic acids, methylisophthalic acid,  $CH_3 \cdot C_6H_3(COOH)_2$  [ $CH_3 : COOH : COOH = 1 : 2 : 4$ ], methylterephthalic acid,



and also nitro-derivatives of these acids and of pseudocumene, and as the separation of these various substances by the method given by Fittig and Laubinger is exceedingly tedious, many experiments were made, in the hope of being able to devise a more simple method for preparing these acids.

In the first place, pseudocumene was brominated at  $150^\circ$  and the bromo-derivative  $C_6H_3(CH_3)_2 \cdot CH_2Br$  converted into the ethylic ether  $C_6H_3(CH_3)_2 \cdot CH_2 \cdot OC_2H_5$  by treatment with sodium ethoxide, this was then oxidised in the way recommended by Kipping (*Trans.*, 1888, 53, 45) for preparing isophthalic acid, but the results were not satisfactory, and as the irritating vapours of the bromopseudocumene made the process very objectionable, it was abandoned.

The next method of preparing paraxylic acid which was investigated was that devised by Armstrong and Kipping (*Trans.*, 1893, 63, 75), who showed that camphor, when digested with sulphuric acid yields acetyl-2-ortho-xylene [ $Me_2 : Ac = 1 : 2 : 4$ ], and that this, on oxidation with nitric acid, yields pure paraxylic acid. We, however, soon found that this method is not suitable for the preparation of large quantities of the acid, owing to the difficulty of obtaining acetyl-2-ortho-xylene in a sufficiently pure condition for giving good results on oxidation.

Ultimately, we found it necessary to return to the oxidation of pseudocumene with nitric acid, but it very soon became evident that some improvement must be made in the method of separating the products of oxidation, in order to obtain sufficient material for this investigation.

The chief objection to Fittig and Laubinger's process is the distillation in steam which they recommend as a means of partially separating the oxidation products, because the xylic acids volatilise with difficulty in steam, and therefore, when working with large quantities of



material, this operation takes a considerable length of time and involves the evaporation of large quantities of liquid ; even then, the products obtained are in a very impure condition.

Several experiments were made with the object of avoiding this steam distillation, and ultimately the following method was devised, which was found to work well.

After oxidising the pseudocumene in the way recommended by Fittig and Laubinger, the semi-solid product is dissolved in an excess of sodium carbonate, and the nitro-compounds and unaltered pseudocumene removed by extraction with ether. The alkaline solution is then acidified, and the precipitated acids, collected by means of the pump, are dried and converted into their methylic salts, which are then fractionated under reduced pressure.

In this way, two principal fractions are obtained, namely, one boiling at 140—160° (40 mm.), which contains the methylic salts of the two xylic acids, and the other boiling at 180—200° (40 mm.), consisting principally of the mixed methylic salts of methylisophthalic acid and methylterephthalic acids ; the former fraction always remained liquid, whilst the latter quickly solidified.

The fraction 140—160° (40 mm.) is hydrolysed, the mixed xylic acids thus obtained are converted into their calcium salts, and the latter are then separated by repeated recrystallisation from water ; the separation of methylisophthalic acid and methylterephthalic acid is described later on in this paper.

In our first experiments on the reduction of the xylic acids, the action of sodium amalgam on paraxylic acid was investigated, but even when the alkaline solution of the acid was boiled with sodium amalgam in the way recommended by Aschan (*Annalen*, 1892, 271, 234) very little action took place, and nearly all the acid was recovered unchanged. This method was then abandoned, and the reduction of xylic acid and paraxylic acid with sodium and isoamylic alcohol was next tried and found to give satisfactory results, the acids being converted in this way always into a mixture of the tetrahydro- and hexahydro-derivatives ; it was not found possible to reduce the whole of the acid to the hexahydro-derivative, although many experiments were made with this object under very varying conditions, as even after the acids had been subjected repeatedly to the action of the reducing agent, a considerable quantity of tetrahydro-acid was always present.

As a rule, after several successive treatments with sodium and isoamylic alcohol, the reduced acid, in each case, was found to contain 50—60 per cent. of the hexahydro- and 40—50 per cent. of the tetrahydro-derivative. On fractionation, the mixed acids distil in each case at about 160—170° (40 mm.), and the purified product, when left

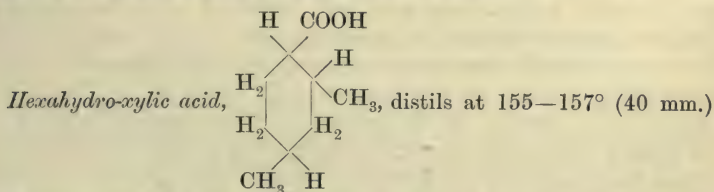
for some time in a freezing mixture, deposits small quantities of solid acid which, on examination, proved to be the tetrahydro-acid.

*Tetrahydroparaxylic acid*,  $C_9H_{14}O_2$ , melts at  $83^\circ$ , and unites with bromine, forming dibromhexahydroparaxylic acid,  $C_9H_{14}Br_2O_2$ , which melts at  $124^\circ$ .

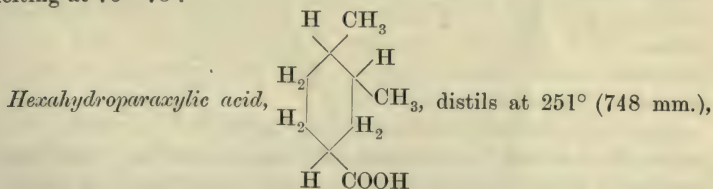
*Tetrahydro-xylic acid*,  $C_9H_{14}O_2$ , melts at  $104^\circ$ , and also absorbs bromine.

The oily reduced acid from both reductions, and from which no more crystals could be obtained, still contains a large proportion of the tetrahydro-compound, and attempts were made to convert the whole of it into the hexahydro-acid by repeated reduction with sodium and isoamylic alcohol, and by adding on hydrogen bromide and heating the bromide with zinc dust and acetic acid, but without success.

As we were unable to reduce the acids completely to the hexahydro-derivatives, we decided to separate the hexahydro-acid from the accompanying tetrahydro-acid, and for this purpose we employed two methods, namely, (1) oxidation of the mixture with potassium permanganate, by which means the tetrahydro-acids are converted into syrupy hydroxy-compounds, leaving the hexahydro-acids unchanged; (2) the conversion of the mixed acids into their anilides, by treating the acid chlorides with aniline, and subsequently separating the hexahydro-anilide from the product by fractional crystallisation. The oxidation with permanganate was performed in very dilute and cold solutions, the unaltered hexahydro-acids being subsequently separated from the non-volatile hydroxy-acids by distillation in steam.



as a colourless liquid, which on standing solidifies to colourless crystals melting at  $76-78^\circ$ .



and does not show any signs of crystallisation, even on long standing. The syrupy hydroxy-acids obtained during the above oxidations could not be obtained in a crystalline condition, and as, on further oxidation

with chromic acid, they did not yield any solid products, their examination was not continued further.

It will be seen that, by the above method of separating the hexahydro-acids, the tetrahydro-acids are always destroyed, and as it was especially important to carefully study these tetrahydro-acids and their derivatives the separation by means of the anilides was tried, but with little success. The acids were converted into the anilides in each case, but on subsequent crystallisation only the anilides of the hexahydro-acids could be isolated in any quantity in the pure state. This want of success was apparently due to the presence of a considerable amount of resinous matter, produced, probably, by the action of phosphorus trichloride on the unsaturated tetrahydro-acids; in both cases, however, besides the anilides of the hexahydro-acids, small amounts of other anilides were isolated, but in quantities too small for further identification. The anilide of hexahydroparaxylic acid melts at  $115^{\circ}$ , whilst that of hexahydro-xylic acid melts at  $188^{\circ}$ ; these anilides are best hydrolysed by heating them with a solution of hydrogen chloride in acetic acid, the yield of acid obtained in this way being quantitative. Prepared by this process, hexahydroparaxylic acid still remained liquid, even when cooled to  $-10^{\circ}$ ; hexahydro-xylic acid, however, quickly solidified, forming colourless plates which melted at  $76-78^{\circ}$ : both acids possess a peculiar, pungent smell, somewhat resembling that of the higher fatty acids.

Owing to the difficulty of obtaining the pure tetrahydro-acids in any quantity, experiments were next instituted with the object of preparing these acids from the hexahydro-acids, and in order to do this the hexahydro-acids were brominated, and the monobromo-derivatives, after conversion into the ethereal salts, hydrolysed, in the first place, with alcoholic potash. It was thought that this method might give very interesting results, as very probably the tetrahydro-acids obtained would be isomeric, and not identical with the tetrahydro-acids prepared by the direct reduction of the xylic acids. However, although the experiments were very much varied, instead of the pure tetrahydro-acids, the products in each case were semi-solid, uninviting-looking masses, which evidently contained several substances, and as the quantities at our disposal were small, it was impossible to effect a separation of the various constituents.

Apparently, the tetrahydro-acids first formed by this reaction are in part oxidised during the treatment with potash, because, in our experiments with hexahydroparaxylic acid, an acid was obtained in this way which had the approximate constitution of a dihydroparaxylic acid.

In the case of hexahydro-xylic acid, the bromination did not take place very satisfactorily, as the product, after treatment with alcohol,



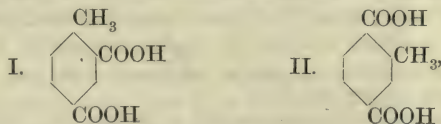
appeared to contain, besides ethylic bromohexahydro-xylate, traces of the ethylic salt of a bromo-xylic acid. The formation of the latter is probably due to the bromine converting part of the hexahydro-acid into xylic acid, which then, by the further action of the bromine, was converted into bromoxylic acid. When the ethereal salts of the bromohexahydro-xylic acids are digested with diethylaniline, they are converted fairly quantitatively into the ethylic salts of the corresponding tetrahydro-acids, which are colourless, sweet-smelling oils, distilling without decomposition at about  $155^{\circ}$  (60 mm.), but these ethereal salts on hydrolysis do not yield the pure tetrahydro-acids; unfortunately, owing to the nature of the product and to the small quantity of material at our disposal, we were unable to investigate this matter further.

Although we have had so much difficulty in obtaining the tetrahydro-derivatives of xylic acid and paraxylic acid in any quantity, we were, nevertheless, able to prepare sufficient of each acid to prove conclusively that these tetrahydro-acids are not identical with the acids which have been obtained by the reduction of the  $\alpha$ - and  $\beta$ -camphylic acids.

This does not, of course, prove that the  $\alpha$ - and  $\beta$ -camphylic acids are not derivatives of the xylic acids, because there are many theoretically possible isomeric tetrahydro-xylic acids which are not described in this paper. As, however, the further study of the camphylic acids has made it appear unlikely that these acids are closely connected with the xylic acids, we have decided, in the meantime, to discontinue these experiments, and to publish the results which have so far been obtained.

*Separation of Methylisophthalic Acid from Methylterephthalic Acid.  
Preparation of Tetrahydromethylterephthalic Acid.*

During the separation of the acids formed by the oxidation of pseudocumene by means of their methylic salts, as explained on page 160, a considerable quantity of a fraction boiling at  $180$ – $200^{\circ}$  (40 mm.) was obtained, and on investigating this product we were ultimately able to show that it consisted of the methylic salts of methylisophthalic acid, I, and methylterephthalic acid, II,



but no methylphthalic acid could be isolated from the mixture. The above fraction, on cooling, solidified to a crystalline mass, melting roughly at  $40$ – $50^{\circ}$ , and by subjecting it to a series of fractional crystallisations, we ultimately succeeded in separating it into two portions, A, melting at  $73$ – $74^{\circ}$ , and B, at about  $58$ – $60^{\circ}$ . Each of these, on analysis, gave



numbers agreeing with the formula  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{COOCH}_3)_2$ , and as further recrystallisation did not appear to affect the melting points, we concluded that they were the pure methylic salts of two distinct dibasic acids of the formula  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{COOH})_2$ .

On hydrolysis with potash, the methylic salt A (m. p. 73—74°) yielded an acid melting at 325—330°,\* which did not form an anhydride and which, in its properties, agreed so closely with methylisophthalic acid,† that we concluded at first that it was identical with this acid, and that the methylic salt A was methylic methylisophthalate.

The methylic salt B (m. p. 58—60°), on hydrolysis, yielded an acid,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{COOH})_2$ , which melted at 293—295° and gave no anhydride, and consequently we supposed it to be *methylterephthalic acid*, especially as Fittig and Laubinger (*Annalen*, 1869, 151, 276) had described methylterephthalic acid as melting at 280—283°, and, after sublimation, at 291°.

On treating the supposed methylisophthalic and methylterephthalic acids with sodium amalgam, it was observed that the acid (m. p. 325—330°) corresponding with the methylic salt A (m. p. 73—74°) was readily and completely reduced to a tetrahydro-acid, whereas the acid (m. p. 293—295°) obtained from the methylic salt B (m. p. 58—60°) was only partially reduced, yielding a tetrahydro-acid which was evidently identical with that obtained from the acid of higher melting point.

The acid which had not been reduced during this treatment was carefully purified, and found to have the formula  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{COOH})_2$ ; it melted now at 320—330°, and yielded a methylic salt which fused sharply at 80°, and which may be called C. This acid is not in the least degree affected by boiling with sodium amalgam, and, as it does not give an anhydride, it must obviously be either methylisophthalic acid or methylterephthalic acid, and the acid which Fittig and Laubinger described as methylterephthalic acid must be a mixture of this acid with methylisophthalic acid, one of which is reduced by sodium amalgam, leaving the other entirely unattacked.

In order to determine which of these two acids is reducible by sodium amalgam, we made a number of experiments, with the object of

\* With regard to the melting point of methylisophthalic acid, compare Claus, *J. pr. Chem.*, 1890, [2], 42, 510.

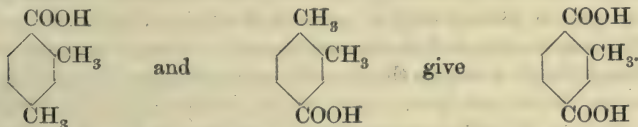
† Methylisophthalic acid has been prepared by Jacobsen (*Ber.*, 1881, 14, 2112) by the oxidation 1:4-dimethylbenzoic acid with permanganate; by Claus (*Ber.*, 1886, 19, 233; *J. pr. Chem.*, 1890, [2], 42, 509) by the oxidation of methyl cymyl ketone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{CH}_3) \cdot \text{C}_3\text{H}_7$ , and of the acid



and by Hjelt and Gadd (*Ber.*, 1886, 19, 868) by the oxidation of pseudocumenyl alcohol,  $\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{CH}_2 \cdot \text{OH})_2$ .

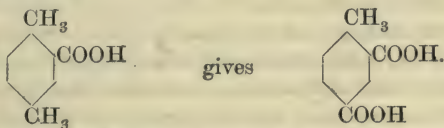
deciding which of the two acids formed a methylic salt melting at 73—74°, and which a methylic salt melting at 80°.

By oxidising xylic acid and paraxylic acid with potassium permanganate, we obtained, in both cases, an acid melting at 325—330° which did not give an anhydride, and which must, therefore, be *methylterephthalic acid*.



As the methylic salt of this acid melts at 73—74°, it follows that the methylic salt A is *methylic terephthalate*.

When iso-xylic acid is oxidised with permanganate, it yields a dibasic acid which does not form an anhydride, and which must, therefore, be *methylisophthalic acid*.



This acid melts at 320—330°, and yields a methylic salt melting at 80°. The methylic salt C is, therefore, *methylic isophthalate*.

On treatment with sodium amalgam at 100°, methylisophthalic acid remains unchanged, whereas, on the other hand, methylterephthalic acid, under the same conditions, is apparently completely reduced to a tetrahydro-derivative.

*Tetrahydromethylterephthalic acid*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_7(\text{COOH})_2$ , is moderately easily soluble in water, and melts at 240—245°; it yields a dimethylic salt,  $\text{CH}_3 \cdot \text{C}_6\text{H}_7(\text{COOCH}_3)_2$ , which is a colourless oil boiling at 165—170° (20 mm.).

Although the solution of the acid in sodium carbonate very quickly decolourises permanganate, yet the free acid does not appear to absorb bromine or hydrogen bromide at all readily. When heated with a saturated solution of hydrogen bromide in glacial acetic acid at 100° in a sealed tube, it yields a black, oily mass containing bromine, but which could not be purified. Experiments on the reduction of this crude hydrobromide with zinc dust and acetic acid were instituted, but we have so far not been able to isolate the hexahydromethylterephthalic acid, which should be formed in this way.

#### EXPERIMENTAL.

*Oxidation of Pseudocumene*.—For this purpose, as stated in the introduction, we employed a modification of the process devised by

Fittig and Laubinger (*Ann.*, 1869, **151**, 269), their method of separating the products by distilling in a current of steam being very troublesome and inconvenient when working with large quantities.

As the result of numerous experiments, we ultimately adopted the following method in preparing the acids required for this research. Pseudocumene (250 grams), mixed with dilute nitric acid (700 grams of acid, sp. gr. 1.4, diluted with  $2\frac{1}{2}$  volumes of water), is heated to boiling for 18 hours in a large flask connected with a reflux condenser. The cold liquid is then largely diluted, the semi-solid precipitate collected with the aid of the pump, washed well with water, and dissolved in a solution of sodium carbonate. The nitro-compounds and unaltered pseudocumene which remain undissolved are removed by agitation with ether, and the aqueous solution is heated to boiling and acidified with hydrochloric acid. The precipitate thus obtained is collected, washed with water, and after being pressed on porous plates to remove oily matter, is dried at  $100^{\circ}$ . The mixed acids are then converted into their methylic salts by saturating their solution in methylic alcohol with dry hydrogen chloride; the mixed methylic salts, after being precipitated with water and extracted with ether, &c., in the usual way, are fractionated several times under a pressure of 40 mm. Of the two fractions obtained, the larger distilling at  $140\text{--}155^{\circ}$ , consists principally of the methylic salts of xylic and paraxylic acids; whilst the smaller fraction, which distils at  $180\text{--}200^{\circ}$ , and quickly solidifies on cooling, contains the methylic salts of methylterephthalic and methylisophthalic acids. A third, but very small, fraction, boiling at  $250\text{--}270^{\circ}$ , was also obtained; this was a very viscid liquid, which possibly contained the methylic salts of trimellitic acid, but it was not further investigated.

*Separation of the Xylic and Paraxylic Acids.*—In order to isolate these acids, the fraction (135 grams) containing their methylic salts is hydrolysed by boiling with a solution of alcoholic potash (80 grams) in a reflux apparatus for 3 hours, the alcohol distilled off, the residue dissolved in water, and the solution evaporated to a moderately small bulk. While still hot, this is acidified with hydrochloric acid, and the precipitate, which is somewhat oily at first, but on cooling becomes quite hard, is first roughly freed from oily matter and other impurities by crystallisation from acetic acid; if this is not done, the subsequent separation of the isomerides by means of their calcium salts becomes a very difficult matter. The mixture of acids which separates from the hot, concentrated solution in glacial acetic acid in the form of a crystalline precipitate melting roughly at  $105^{\circ}$ , is collected, washed first with acetic acid and then with water, and dissolved in a slight excess of hot sodium carbonate solution; on mixing



this with a strong, hot solution of rather more than the calculated quantity of calcium chloride, and cooling, a mixture of the calcium salts of the two xylic acids separates almost completely; the salts, after being collected and washed with a little water, are crystallised from a considerable quantity of boiling water. If the acids are purified as described above, the first crystallisation yields the almost pure calcium salt of paraxylic acid, this being the least soluble. It is, however, a matter of considerable difficulty to separate the calcium salts contained in the mother liquor, but this may be effected in the following manner. When the solutions of the calcium salts have yielded as much pure calcium paraxylate as possible, the mother liquors are acidified, and the precipitated acids collected and crystallised from acetic acid. A considerable quantity of nearly pure xylic acid separates first in beautiful, long needles. After this has been collected, and the acetic acid removed from the mother liquors by distillation, the acids are again converted into the calcium salts and crystallised from water. By a repetition of this process, it is possible to separate the whole of the material into calcium paraxylate and xylic acid. The paraxylic acid obtained from the pure calcium salts by precipitation with hydrochloric acid was recrystallised from acetic acid. Xylic acid,  $C_6H_3(CH_3)_2 \cdot COOH$  [ $CH_3:CH_3:COOH = 1:3:4$ ], crystallises from acetic acid in beautiful, long, prismatic needles melting at  $126^\circ$ .

Paraxylic acid, [ $CH_3:CH_3:COOH = 1:2:4$ ], crystallises in short needles melting at  $163^\circ$ .

*Tetrahydroparaxylic acid,  $C_9H_{14}O_2$ .*

As stated in the introduction, this acid is one of the products of the reduction of paraxylic acid by means of sodium and isoamylic alcohol. Pure paraxylic acid (30 grams) is dissolved in isoamylic alcohol ( $1\frac{1}{2}$  litres) contained in a large, round-bottomed flask attached to a long reflux condenser. The liquid is heated to the boiling point, and then sodium (10 grams) is dropped in; a violent action takes place, and as soon as this has subsided more sodium (20 grams) is added. When the sodium has all dissolved (the mixture being heated if necessary), the contents of the flask are allowed to cool, diluted with water and acidified with hydrochloric acid; the liquid then separates into two layers, the upper of which is isoamylic alcohol containing the organic acid in solution. The lower layer, consisting of sodium chloride solution and some hydrochloric acid, is shaken with pure isoamylic alcohol, in order to extract any traces of the organic acid which it may contain, and the whole of the isoamylic alcohol solution is dehydrated by distillation until the temperature of the vapour rises to  $120^\circ$ . It is then treated with sodium (30 grams) exactly as before, and the process of



extraction again repeated. After thrice treating with sodium, the product is diluted with a large quantity of water, the upper layer of isoamylic alcohol is distilled almost to dryness, and the residue dissolved in water and mixed with the aqueous layer. If this is not done, there is a very considerable loss of product, as the isoamylic alcohol retains a quantity of the sodium salts of the reduced acids, even after it has been repeatedly washed with water. The aqueous solution, after being boiled until free from isoamylic alcohol, is acidified and extracted with pure ether, the ethereal solution is dried over calcium chloride, the ether distilled off, and the oily residue fractionated under diminished pressure. Nearly the whole distils at about  $160-170^{\circ}$  under a pressure of 40 mm. When, however, about three-quarters of the acid has distilled, the receiver is changed and the last portion collected separately; the latter, when exposed to the cold for about a week, deposits crystals of tetrahydroparaxylic acid, whereas the first fraction if similarly treated yields very few crystals. The crystals were collected with the aid of the pump, pressed on a porous plate, and recrystallised several times from light petroleum (b. p.  $60-80^{\circ}$ ).

I. 0.1020 gave 0.2618  $\text{CO}_2$  and 0.0830  $\text{H}_2\text{O}$ . C = 70.00; H = 9.04.

II. 0.1096 ,, 0.2820  $\text{CO}_2$  ,, 0.0900  $\text{H}_2\text{O}$ . C = 70.17; H = 9.12.

$\text{C}_6\text{H}_7(\text{CH}_3)_2\cdot\text{COOH}$  requires C = 70.13; H = 9.09 per cent.

*Tetrahydroparaxylic acid* crystallises in prisms melting at  $83^{\circ}$ . It is easily soluble in benzene, alcohol, ether, and acetic acid; sparingly so in cold, easily in hot, light petroleum. Its solution in sodium carbonate immediately reduces potassium permanganate in the cold, and bromine is quickly absorbed by a solution of the acid in chloroform.

The yield of reduced acid, after distillation, was usually about 75 per cent. of the theoretical quantity, but of this only about 10 per cent. separated in the form of crystals of tetrahydroparaxylic acid.

*Dibromhexahydroparaxylic Acid*,  $\text{C}_9\text{H}_{14}\text{Br}_2\text{O}_2$ .

This was prepared by dissolving pure tetrahydroparaxylic acid in dry chloroform and adding a chloroform solution of bromine until the colour of the bromine remained permanent. The oil which was deposited, on allowing the chloroform to evaporate spontaneously, slowly solidified. This crude product purified by recrystallisation from dilute acetic acid saturated with hydrogen bromide, separated in colourless plates melting at  $124^{\circ}$

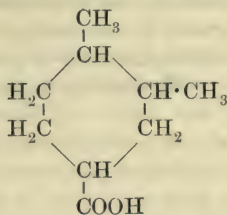
0.0532 gave 0.0640 AgBr. Br = 51.17.

$\text{C}_9\text{H}_{14}\text{Br}_2\text{O}_2$  requires Br = 50.95 per cent.

*Dibromhexahydroparaxylic acid* melts at  $124^{\circ}$ . It dissolves readily in most organic solvents on boiling, being apparently decomposed at the same time, as we could not succeed in recovering it from them

a crystalline form. It separates, however, readily from dilute acetic acid if decomposition is prevented by previously saturating the solution with hydrogen bromide.

*Hexahydroparaxylic acid*,  $C_6H_9(CH_3)_2 \cdot COOH$ ,



This acid is formed when paraxylic acid is reduced by sodium and isoamylic alcohol as explained on page 167, and is present in considerable quantities in the mother liquor of the reduced acid after the bulk of the crystalline tetrahydroparaxylic acid has been removed by cooling in a freezing mixture.

In order to isolate it, two methods were employed.

1. The crude product was treated with permanganate so as to oxidise the tetrahydroparaxylic acid, the hexahydroparaxylic acid remaining unchanged.

2. The mixed acids were converted into the anilides, and these separated by fractional crystallisation.

*Method I.*—The oxidation was carried out in the following manner. The oily mixture of tetrahydro- and hexahydro-paraxylic acids was dissolved in a small quantity of sodium carbonate solution, diluted with a large quantity of water, and oxidised by running in slowly a weak solution of potassium permanganate. During the whole operation, a rapid current of carbon dioxide was passed through the liquid, which was vigorously stirred by means of a turbine, and kept cold by adding ice from time to time. When the colour of the permanganate remained permanent, the liquid was mixed with a little alcohol, boiled, and the manganese dioxide filtered off, well washed with hot water, and the filtrate evaporated to a small bulk. This was then acidified and subjected to distillation in a rapid current of steam until the condensed water was quite clear and had only a very slight acid reaction. The distillate was extracted three times with ether, and the oily residue left on evaporating the dried ethereal solution was fractionated at the ordinary pressure. Nearly the whole distilled at  $251^\circ$  (748 mm.) as a colourless oil which gave the following results on analysis.

0.1480 gave 0.3760  $CO_2$  and 0.1336  $H_2O$ .  $C = 69.28$  ;  $H = 10.03$ .

$C_6H_9(CH_3)_2 \cdot COOH$  requires  $C = 69.23$  ;  $H = 10.25$  per cent.

Hexahydroparaxylic acid is an oil of peculiar odour, somewhat similar to that of the higher fatty acids; it remains liquid even when cooled to a temperature of  $-10^{\circ}$ .

*Method II.*—The separation of hexahydroparaxylic acid by means of its anilide was conducted as follows. The crude mixture of acids (30 grams) was first converted into the acid chlorides by heating with phosphorus trichloride (15 grams) in a reflux apparatus for 10 minutes; the liquid was then decanted from the layer of phosphorus acid, and distilled under reduced pressure. The fraction boiling at  $135\text{--}145^{\circ}$  (60 mm.) was dissolved in pure, dry ether, and slowly mixed with an ethereal solution of aniline (60 grams); after standing some time, water was added, the ethereal solution separated, washed with dilute hydrochloric acid until free from aniline, dried, and the ether distilled off. The oily residue, on standing, quickly solidified, and the product, after two crystallisations from light petroleum (b. p.  $100\text{--}120^{\circ}$ ), was obtained in colourless prisms melting at  $115^{\circ}$ . This substance is the anilide of hexahydroparaxylic acid, as was proved by comparing it with a sample of the anilide prepared from the pure acid. In order to obtain the hexahydro-acid from its anilide, the latter is heated for 12 hours at  $150^{\circ}$  in a sealed tube with acetic acid saturated with hydrogen chloride, and containing a little aqueous hydrochloric acid. The product was then diluted with water and extracted several times with ether. In order to remove the aniline, the ethereal solution was shaken with excess of sodium carbonate solution, and the alkaline liquid acidified and again extracted with ether. This ethereal solution was washed, dried, and evaporated, the oily residue being purified by fractional distillation. Even when prepared from the pure anilide in this way, hexahydroparaxylic acid is an oil which does not solidify, even at low temperatures. The yield of hexahydroparaxylic acid obtained from the crude mixture of acids by this method is from 30 to 40 per cent.

The petroleum mother liquors of the anilide of hexahydroparaxylic acid, after the removal of the light petroleum by distillation, deposited an oil from which a small quantity of solid separated on standing. This, after being crystallised from petroleum, melted at  $140\text{--}145^{\circ}$ ; the quantity, however, was too small for further examination.

The attempts made with the object of obtaining tetrahydroparaxylic acid from the oily anilide which remained after the above crystalline products had been extracted as completely as possible, were unsatisfactory.

*Hexahydroparaxylyl chloride*,  $\text{C}_6\text{H}_9(\text{CH}_3)_2 \cdot \text{COCl}$ .

This was prepared by gently heating pure hexahydroparaxylic acid (4 grams) with phosphorus trichloride (2 grams) for 10 minutes; the liquid was decanted from the phosphorous acid and distilled under reduced pressure. It is a disagreeably-smelling liquid boiling at  $110^{\circ}$  (25 mm.).



0.2406 gave 0.1996 Ag Cl. Cl = 20.52.

$C_8H_{15} \cdot COCl$  requires Cl = 20.34 per cent.

*Ethyl hexahydroparaxylylate*,  $C_6H_9(CH_3)_2 \cdot COOC_2H_5$ .

This was prepared by pouring the acid chloride into three times its volume of alcohol, and after allowing it to stand a short time, diluting with water, extracting with ether, &c. The brownish oil thus obtained was purified by fractional distillation. Ethyl hexahydroparaxylylate is an oil of pleasant odour, and lighter than water; it boils at  $224^\circ$  (758 mm.).

0.1272 gave 0.3334  $CO_2$  and 0.1210  $H_2O$ . C = 71.48; H = 10.65.

$C_8H_{15} \cdot COOC_2H_5$  requires C = 71.74; H = 10.87 per cent.

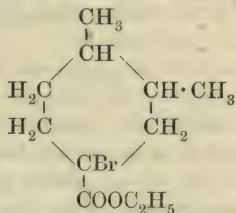
*Anilide of hexahydroparaxylic acid*,  $C_8H_{15} \cdot CO \cdot NH \cdot C_6H_5$ .

This anilide was prepared by mixing ethereal solutions of equal quantities of the acid chloride and aniline. After standing for some time, water was added, and the ethereal solution washed first several times with small quantities of dilute hydrochloric acid until free from aniline, and then once with water. It was then dried and the ether distilled off; the oily residue gradually solidified, and after being purified by crystallisation from light petroleum (b. p.  $80-100^\circ$ ) the anilide was obtained in prisms melting at  $115^\circ$ . Analysis; found

N = 6.39;  $C_8H_{15} \cdot CO \cdot NH \cdot C_6H_5$  requires N = 6.06.

The anilide of hexahydroparaxylic acid is moderately soluble in benzene and alcohol, but only slightly in cold light petroleum (b. p.  $80-100^\circ$ ), although it dissolves readily in the boiling solvent.

*Ethyl bromhexahydroparaxylylate*,  $C_6H_8Br(CH_3)_2 \cdot COOEt$



This was prepared, for reasons explained in the introduction, by brominating hexahydroparaxylic acid and subsequently pouring the product into absolute alcohol.

Hexahydroparaxylic acid (5 grams) was carefully mixed with phosphorus pentabromide (5 grams) and bromine (6 grams), and gently heated on the water bath until the bromine had disappeared. The product, poured into twice its volume of alcohol, was allowed to stand for some time, and then diluted with water, the heavy oil which



separated being extracted with ether, &c., in the usual manner. The residue thus obtained, when fractionated under reduced pressure, yielded ethylic bromhexahydroparaxylate as a heavy oil boiling without decomposition at 170—180° (55 mm.); the yield was about 70—80 per cent.

0.1928 gave 0.1376 AgBr. Br = 30.37.

$C_8H_{14}Br \cdot COOC_2H_5$  requires Br = 30.42 per cent.

When hydrolysed with potash, this ethereal salt yields a mixture of acids, a behaviour which is probably due in part to the oxidation of the tetrahydroparaxylic acid formed in the first instance. The only substance we were able to isolate from this mixture was a small quantity of a crystalline acid which melted roughly at 135—140°, and on analysis gave numbers corresponding with those required by dihydroparaxylic acid,  $C_9H_{12}O_2$ .

*Ethylic tetrahydroparaxylate*,  $C_6H_7(CH_3)_2 \cdot COOC_2H_5$ .

This is formed when ethylic bromhexahydroparaxylate is digested with diethylaniline. Pure ethylic bromhexahydroparaxylate mixed with twice its weight of diethylaniline was heated to gentle ebullition for 4 hours, and then poured into dilute hydrochloric acid. The dark-coloured oil which separated was extracted with ether, washed, and treated in the usual way. The product on being fractionated under reduced pressure, yielded a colourless, sweet-smelling oil which distilled at 155° (60° mm.), and on analysis gave numbers showing that it was of ethylic tetrahydroparaxylate.

0.0814 gave 0.2162  $CO_2$  and 0.0720  $H_2O$ . C = 72.43; H = 9.82.

$C_8H_{13} \cdot COOC_2H_5$  requires C = 72.52; H = 9.89 per cent.

In order, if possible, to prepare the corresponding tetrahydroparaxylic acid, the ethylic salt was hydrolysed.

Ethylic tetrahydroparaxylate (3 grams) was heated on the water bath with potash (3 grams) dissolved in methylic alcohol for 2 hours, the alcohol distilled off, the residue evaporated with water until free from alcohol, and then acidified and extracted with ether. The dried ethereal solution, on distillation, left an oil which partially solidified. The crystals, after being pressed upon a porous plate and crystallised from light petroleum (b. p. 100—120°), formed prisms melting at 135—140°, and on analysis gave numbers agreeing with the formula  $C_9H_{12}O_2$ .

0.1180 gram gave 0.3068  $CO_2$  and 0.0842  $H_2O$ . C = 71.14; H = 7.93.

$C_9H_{12}O_2$  requires C = 71.05; H = 7.88.

$C_9H_{14}O_2$  requires C = 70.13; H = 9.09 per cent.

This substance is, therefore, probably a dihydroparaxylic acid identical with the substance described above.

*Reduction of Xylic Acid.*

The reduction of xylic acid with sodium and isoamylic alcohol, and the methods used in the separation of the acids thus formed, were conducted in almost exactly the same manner as in the case of paraxylic acid; a brief description of the process, therefore, is all that is needful.

Pure xylic acid (30 grams), dissolved in isoamylic alcohol ( $1\frac{1}{2}$  litres), was heated to boiling and treated three times in succession with sodium (30 grams), the same precautions and methods of extraction being adopted as in the reduction of paraxylic acid. The oily acid thus obtained when fractionated under reduced pressure passed over entirely at about  $160\text{--}170^\circ$  (40 mm.). When three-quarters of the acid had distilled, the last portion was collected separately; this soon deposited crystals when exposed to the cold, whilst the first fraction usually remained liquid.

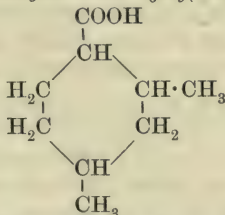
*Tetrahydro-xylic Acid*,  $\text{C}_6\text{H}_7(\text{CH}_3)_2\cdot\text{COOH}$ .

This was obtained from the higher fraction of the reduced xylic acid, the crystals which were deposited being pressed, and recrystallised several times from light petroleum (b. p.  $80\text{--}100^\circ$ ). It forms plates which melt at  $103^\circ$ .

0.1000 gave 0.2570  $\text{CO}_2$  and 0.0830  $\text{H}_2\text{O}$ .  $\text{C} = 70.09$ ;  $\text{H} = 9.22$ .

$\text{C}_6\text{H}_7(\text{CH}_3)_2\cdot\text{COOH}$  requires  $\text{C} = 70.13$ ;  $\text{H} = 9.09$  per cent.

Tetrahydro-xylic acid is readily soluble in benzene, alcohol, and acetic acid; sparingly so in cold petroleum, but very soluble in the hot solvent. When dissolved in sodium carbonate solution, it instantly decolorises potassium permanganate; its solution in chloroform also decolorises bromine very readily, but, unfortunately, we were not able to isolate the product owing to the small amount of material at our disposal.

*Hexahydro-xylic Acid*,  $\text{C}_6\text{H}_9(\text{CH}_3)_2\cdot\text{COOH}$ .

This acid, like the corresponding hexahydroparaxylic acid, was isolated from the mixture of reduced acids by two processes, viz., (1) oxidation with potassium permanganate, and (2) hydrolysis of the anilide. The second method gives the purer product. In both cases, a liquid is obtained which, when prepared from the anilide, solidifies quickly, whereas the product obtained by oxidation solidifies but slowly and very incompletely.

0.1694 gave 0.4288  $\text{CO}_2$  and 0.1568  $\text{H}_2\text{O}$ .  $\text{C} = 69.03$ ;  $\text{H} = 10.28$ .

$\text{C}_6\text{H}_9(\text{CH}_3)_2\text{COOH}$  requires  $\text{C} = 69.23$ ;  $\text{H} = 10.25$  per cent.

Hexahydro-xylic acid crystallises from light petroleum ( $100\text{--}120^\circ$ ) in thick plates melting at  $76\text{--}78^\circ$ . It boils at  $250\text{--}255^\circ$ , and is readily soluble in benzene, alcohol, and acetic acid; sparingly in cold, easily in hot, light petroleum. Its solution in cold dilute sodium carbonate decolorises permanganate only very slowly.

*Anilide of Hexahydro-xylic Acid*,  $\text{C}_6\text{H}_9(\text{CH}_3)_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ .

This anilide was obtained from reduced xylic acid, and employed for the preparation of the foregoing hexahydro-xylic acid.

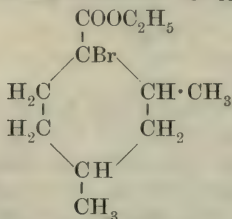
Reduced xylic acid (28 grams) was heated for about 15 minutes with phosphorus trichloride (14 grams), and the liquid decanted from the phosphorous acid and distilled under reduced pressure; the acid chloride (30 grams), which came over at about  $130\text{--}140^\circ$  (40 mm.), was then dissolved in pure, dry ether, and carefully added to an ethereal solution of aniline (56 grams); after a short time water was added and the ethereal solution washed, dried, &c., as before. The oil obtained in this way soon solidified, and after being four times recrystallised from a mixture of alcohol and petroleum (b.p.  $100\text{--}120^\circ$ ), was obtained in needles melting at  $180^\circ$ .

On analysis, nitrogen was found = 6.26 per cent.;  $\text{C}_8\text{H}_{15}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 6.06$  per cent.

The *anilide of hexahydro-xylic acid* is sparingly soluble in cold benzene and alcohol, but dissolves readily in these solvents on boiling; it is almost insoluble in cold petroleum (b.p.  $100\text{--}120^\circ$ ) and only sparingly soluble in the hot solvent. These properties, together with its unusually high melting point, distinguish this anilide from the corresponding anilide of hexahydroparaxylic acid.

It is hydrolysed on heating with an acetic acid solution of hydrogen chloride in a sealed tube for 12 hours at  $150^\circ$ , an almost quantitative yield of hexahydro-xylic acid being produced.

*Ethylic bromhexahydro-xylate*,  $\text{C}_8\text{H}_{14}\text{Br}\cdot\text{COOC}_2\text{H}_5$ .



This was prepared in the same manner as the isomeric ethylic bromhexahydroparaxylate. The specimen prepared boiled at  $160\text{--}170^\circ$



(40 mm.), but was apparently not quite pure and probably contained traces of the ethylic salt of bromo-xylic acid,  $C_8H_8Br \cdot COOC_2H_5$ . We were led to these conclusions from the fact that a bromine determination gave too high a result, and, secondly, that the oil on hydrolysis with potash yielded a small quantity of a solid acid which melted at  $170^\circ$  and contained bromine, apparently a monobromo-xylic acid.

The ethylic bromhexahydro-xylate, prepared as explained above, gave the following results on analysis.

0.3010 gave 0.2222 AgBr.  $Br = 31.41$ .

$C_8H_{14}Br \cdot COOC_2H_5$  requires  $Br = 30.42$  per cent.

*Ethylic tetrahydro-xylate*,  $C_8H_{13} \cdot COOC_2H_5$ .

This was obtained by the action of diethylaniline on the bromethereal salt just described. It is a pleasant-smelling liquid boiling at  $228^\circ$  (752 mm.).

0.1293 gave 0.3418  $CO_2$  and 0.1122  $H_2O$ .  $C = 72.02$   $H = 9.64$ .

$C_8H_{13} \cdot COOC_2H_5$  requires  $C = 72.52$ ;  $H = 9.89$  per cent.

A small quantity of this ethylic salt was hydrolysed with potash and yielded an acid melting at  $98-110^\circ$ , but the quantity was insufficient for further examination.

*Preparation of Methylisophthalic Acid and of Methylterephthalic Acid.*

As was explained in the introduction, the oxidation of pseudocumene with dilute nitric acid gives rise to two dibasic acids, namely, methylisophthalic acid,  $CH_3 \cdot C_6H_3(COOH)_2$  [ $CH_3 : COOH : COOH = 1 : 2 : 4$ ], and methylterephthalic acid, and when the acids contained in the crude product of the oxidation are converted into their methylic salts and these are fractionated (see p. 160), the fraction  $180-200^\circ$  (40 mm.), consists almost entirely of the methylic salts of these two acids. This fraction solidifies on cooling, and the solid mass, when subjected to a series of crystallisations from methylic alcohol, separates into two portions, A, the least soluble, melting at  $73-74^\circ$ , and B, which melts at about  $58-60^\circ$ . The melting point of the fraction B does not rise on further crystallisation, and it was, therefore, at first supposed that this substance was pure, especially as, on analysis, it gave numbers agreeing closely with those required by the formula  $CH_3 \cdot C_6H_3(COOCH_3)_2$ .

0.1280 gave 0.2986  $CO_2$  and 0.0686  $H_2O$ .  $C = 63.62$ ;  $H = 5.95$ .

$CH_3 \cdot C_6H_3(COOCH_3)_2$  requires  $C = 63.46$ ;  $H = 5.76$  per cent.

Further experiments showed, however, that it is a mixture of methylic methylisophthalate and methylic methylterephthalate, and the only way which we could find to separate the methylisophthalic from the methylterephthalic acid was by treatment with sodium amalgam.



*Methylisophthalic Acid*,  $[\text{CH}_3 : (\text{COOH})_2 = 1 : 2 : 4]$ .

In order to prepare this acid, the methylic salts B, melting at  $58-60^\circ$  (70 grams) were dissolved in alcohol, mixed with an alcoholic solution of potash (65 grams), and heated on the water bath for 2 hours. The alcohol was then distilled off, the residue diluted with water, evaporated until entirely free from alcohol, and the aqueous solution, after filtration, was acidified; the copious, flocculent precipitate which separated was collected with the aid of the pump, washed well with water, and dried, first on porous plates, and then at  $100^\circ$ . It melted at  $285-290^\circ$ , but on repeated recrystallisation from glacial acetic acid the melting point rose to  $293-295^\circ$ , but no higher. This substance is a mixture of methylisophthalic and methylterephthalic acids, and in order to obtain the former acid from it in a pure state, the mixture, in quantities of 10 grams at a time, was dissolved in sodium carbonate solution in a strong porcelain beaker and 3 per cent. sodium amalgam (1 kilo.) added in quantities of 100 grams at a time. The temperature of the reaction was kept at about  $100^\circ$  by immersing the beaker in a boiling water bath, a rapid current of carbon dioxide was also passed into the mixture during the whole operation, and the separation of sodium salts was prevented by the addition from time to time of small quantities of boiling water.

When the sodium amalgam had all been used up, the aqueous solution was decanted from the mercury, filtered, and acidified; the bulky precipitate then thrown down consisted of nearly pure methylisophthalic acid, as the tetrahydromethylterephthalic acid which is formed during the reduction is soluble in water, and remains dissolved in the mother liquor. The precipitate was collected with aid of the pump, washed well with water, dried first on a porous plate, and then at  $100^\circ$ , and purified by conversion into the methylic salt.

For this purpose, the well-powdered dry acid was suspended in methylic alcohol, the mixture saturated with hydrogen chloride and allowed to stand for some hours; water was then added and the methylic salt extracted with ether. The ethereal solution, after being washed with water and sodium carbonate solution, was dried over calcium chloride, and the ether distilled off, when an oil was left which quickly solidified. After crystallising three times from methylic alcohol, the methylic salt was obtained pure in the form of prismatic needles, which, when heated in a capillary tube, sintered somewhat at  $77^\circ$ , and melted at  $80^\circ$ .

I. 0.1592 gave 0.3710  $\text{CO}_2$  and 0.0864  $\text{H}_2\text{O}$ . C = 63.55; H = 6.03.

II. 0.1172 „ 0.2726  $\text{CO}_2$  „ 0.0628  $\text{H}_2\text{O}$ . C = 63.43; H = 5.95.

$\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{COOCH}_3)_2$  requires C = 63.46; H = 5.76 per cent.

*Methylic methylisophthalate* is readily soluble in most of the ordinary organic solvents, it is, however, but sparingly soluble in cold methylic

or ethylic alcohol, although it dissolves readily in these solvents on boiling. On hydrolysis with potash, it yields pure *methylisophthalic acid*, which separates from acetic acid as a white, apparently amorphous, powder, and melts at about 320—330°.

0.1188 gave 0.2618 CO<sub>2</sub> and 0.0480 H<sub>2</sub>O. C = 60.01; H = 4.48.

CH<sub>3</sub>·C<sub>6</sub>H<sub>3</sub>(COOH)<sub>2</sub> requires C = 60.00; H = 4.44 per cent.

Methylisophthalic acid is practically insoluble in most organic solvents; it dissolves slightly, however, in boiling water, and, on cooling, separates almost completely in white, flocculent masses. When treated with acetic anhydride or acetyl chloride, it does not yield an anhydride. Prolonged treatment with sodium amalgam does not appear to have any action on this acid, nearly the whole being recovered unchanged on acidifying the alkaline product of the reaction.

In purifying methylisophthalic acid in the way described above, the tetrahydroterephthalic acid formed during the reduction remains dissolved in the liquors from which the former acid separates on acidification. To obtain this tetrahydro-acid, the solution was evaporated to dryness, and the residue extracted with ether in a Soxhlet apparatus; after distilling off the ether and crystallising the extract from water, pure tetrahydromethylterephthalic acid was obtained, melting at 240—245° (see p. 178).

0.1110 gave 0.2386 CO<sub>2</sub> and 0.0642 H<sub>2</sub>O. C = 58.62; H = 6.42.

CH<sub>3</sub>·C<sub>6</sub>H<sub>7</sub>(COOH)<sub>2</sub> requires C = 58.69; H = 6.52 per cent.

*Methylterephthalic Acid*, [Me : (COOH)<sub>2</sub> = 1 : 2 : 5]

The methylic salt A, the preparation of which is given on p. 163, consists of pure methylic methylterephthalate.

0.1052 gave 0.2450 CO<sub>2</sub> and 0.0540 H<sub>2</sub>O. C = 63.51; H = 5.70.

CH<sub>3</sub>·C<sub>6</sub>H<sub>3</sub>(COOCH<sub>3</sub>)<sub>2</sub> requires C = 63.46; H = 5.76 per cent.

*Methylic methylterephthalate* is very readily soluble in benzene, ethylic acetate, light petroleum, and hot alcohol, but comparatively sparingly in cold methylic or ethylic alcohol. It melts at 73—74°. In order to prepare methylterephthalic acid, the pure methylic salt (7 grams) was dissolved in alcohol, and heated on the water bath with alcoholic potash (7 grams) for 2 hours. The product was diluted with water, evaporated until free from alcohol, filtered, and acidified, when a very voluminous precipitate was thrown down. This was collected with the aid of the pump, washed well with water, dried, and purified by crystallisation from hot glacial acetic acid, from which it separates as an apparently amorphous powder melting at 325—330°.

0.1106 gave 0.2420  $\text{CO}_2$  and 0.0458  $\text{H}_2\text{O}$ .  $\text{C} = 59.67$  ;  $\text{H} = 4.61$ .

$\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{COOH})_2$  requires  $\text{C} = 60.00$  ;  $\text{H} = 4.44$  per cent.

*Methylterephthalic acid* resembles methylisophthalic acid very closely in its properties. It is practically insoluble in most organic solvents, such as benzene, chloroform, light petroleum, and ether, and although more readily soluble in boiling xylene and glacial acetic acid, it is practically insoluble in these solvents in the cold. When heated, it sublimes without forming an anhydride. Methylterephthalic acid is moderately easily reduced when its solution in sodium carbonate is boiled with sodium amalgam, and in this respect it differs remarkably from methylisophthalic acid, which does not appear to be affected at all by this treatment.

*Tetrahydromethylterephthalic Acid*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_7(\text{COOH})_2$ .

In order to prepare this acid, methylterephthalic acid (18 grams) was dissolved in a little sodium carbonate solution, heated to about  $100^\circ$  by means of a water bath, and sodium amalgam (2 kilos.) added in small quantities at a time, a current of carbon dioxide being passed through the liquid during the operation. When the sodium amalgam had all been added, the aqueous solution was filtered, acidified, and the precipitate, collected by the aid of the filter-pump, was washed with a little water, and purified by crystallisation from hot water. It is thus obtained apparently in the amorphous condition ; it melts at  $240\text{--}245^\circ$ , sintering at about  $230^\circ$ .

0.1182 gave 0.2554  $\text{CO}_2$  and 0.0696  $\text{H}_2\text{O}$ .  $\text{C} = 58.82$  ;  $\text{H} = 6.53$ .

$\text{CH}_3 \cdot \text{C}_6\text{H}_7(\text{COOH})_2$  requires  $\text{C} = 58.69$  ;  $\text{H} = 6.52$  per cent.

*Tetrahydromethylterephthalic acid* is fairly soluble in organic solvents, and especially readily in glacial acetic acid ; it is easily soluble in hot water, and as it is also fairly soluble in cold water, a considerable quantity remains in the mother liquors after the acid has been collected. This can be recovered by evaporating and extracting the solid residue with ether in a Soxhlet's apparatus (see p. 177).

A solution of the acid in sodium carbonate decolourises potassium permanganate very quickly, but the acid itself appears to have little affinity for bromine or hydrogen bromide.

An attempt was made to prepare the bromhexahydro-acid by heating the tetrahydro-acid with a solution of hydrogen bromide in glacial acetic acid in a sealed tube at  $100^\circ$  for several hours. On diluting the product with water, a black, oily-looking precipitate was obtained, but all attempts to isolate a pure bromhexahydro-acid for it were unsuccessful. When the black mass was dissolved in acetic acid and treated



with zinc dust, a small quantity of what appeared to be impure tetrahydromethylterephthalic acid was obtained. The experiment was repeated several times, and in one instance an acid was obtained which decomposed permanganate only very slowly, and melted at 210—220°; the quantity, however, was too small to permit of further investigation.

*Methylic tetrahydromethylterephthalate*,  $\text{CH}_3 \cdot \text{C}_6\text{H}_7(\text{COOCH}_3)_2$ .

This compound was prepared by saturating a solution of the acid in methylic alcohol with dry hydrogen chloride, and adding water after the mixture had been left for several hours. The oil which separated was extracted with ether, the ethereal solution washed with sodium carbonate and then with water, and dried by calcium chloride; the ether was distilled off and the oily residue distilled under reduced pressure.

0.1676 gave 0.3800  $\text{CO}_2$  and 0.1146  $\text{H}_2\text{O}$ .  $\text{C} = 61.83$ ;  $\text{H} = 7.59$ .

$\text{CH}_3 \cdot \text{C}_6\text{H}_7(\text{COOCH}_3)_2$  requires  $\text{C} = 62.26$ ;  $\text{H} = 7.55$  per cent.

*Methylic tetrahydromethylterephthalate* is an oil possessing comparatively little odour; it boils at 165—170° (20 mm.).

*Preparation of Methylterephthalic Acid by the Oxidation of Xylic Acid and of Paraxylic Acid.*

These experiments were instituted, as explained in the introduction, with the object of obtaining pure methylterephthalic acid for comparison with the acids obtained by the oxidation of pseudocumene.

*Xylic acid* (2 grams) was dissolved in sodium carbonate solution and heated on a water bath with a dilute solution of potassium permanganate (4 grams) until the pink colour had disappeared. The manganese dioxide was then removed by filtration, washed with hot water, and the filtrate evaporated to a small bulk; on acidifying the liquid a voluminous precipitate of methylterephthalic acid was thrown down. This was collected, dried on a porous plate, and crystallised from glacial acetic acid, when it separated as an apparently amorphous powder melting at 320—330°. The acid was converted into its methylic salt by means of methylic alcohol and hydrogen chloride in the usual way; after crystallising from methylic alcohol, it melted at 73—74°, and was found to be identical with the methylic salt of this melting point, already described as methylic methylterephthalate (p. 177).

On oxidising *paraxylic acid* in precisely the same way, an acid was obtained which again melted at 320—330° and yielded a methylic salt melting at 73—74° identical with that obtained from xylic acid. These two experiments prove that this substance, melting at 73—74°, must be the methylic salt of methylterephthalic acid.



*Preparation of Methylisophthalic Acid by the oxidation of Isoxylic Acid.*

The isoxylic acid required for these experiments was obtained by the oxidation of paraxylyl methyl ketone  $(\text{CH}_3)_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_3$ , this being prepared by a method similar to that recommended by Claus and Wollner (*Ber.*, 1885, 18, 1856), namely, by treating a mixture of paraxylene and acetyl chloride with aluminium chloride.

Paraxylene (20 grams) was mixed with acetyl chloride (25 grams) and carbon bisulphide (60 grams), and finely-powdered aluminium chloride (26 grams) was gradually added to the mixture, which was well shaken during the operation. The whole was then heated on the water bath for a few minutes, and afterwards poured on to ice. The oil containing carbon bisulphide was extracted with ether, the ethereal solution washed with sodium carbonate, then with water and dried over calcium chloride; the ether and carbon bisulphide were then distilled off, and the residue fractionated under the ordinary pressure. About 7 grams of an oil boiling at  $220\text{--}230^\circ$ , and consisting of nearly pure paraxylyl methyl ketone, were obtained, and 10 grams of paraxylene were recovered unchanged.

*Oxidation of paraxylyl methyl ketone.*—The fraction boiling at  $220\text{--}230^\circ$  was mixed with about 30 grams of dilute nitric acid (1 vol. of acid, sp. gr. 1.4, and 3 vols. of water) and heated just to boiling for 2 hours. On cooling the mixture, the oily product solidified to a hard mass; this was collected, washed with water, and boiled for a considerable time with sodium carbonate solution. The liquid was filtered from the insoluble matter, extracted once with ether and then acidified; the bulky precipitate thus produced was collected, washed with water, dried on a porous plate, and recrystallised from acetic acid. In this way isoxylic acid,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{COOH}[\text{Me}_2:\text{COOH} = 1:2:4]$ , was obtained quite pure, melting at  $132^\circ$ .

The oxidation of isoxylic acid with permanganate was conducted in exactly the same manner as described in the case of xylic acid (p. 179), and a dibasic acid was obtained which, as it did not give an anhydride, was evidently methylisophthalic acid. It melted at  $320\text{--}330^\circ$ , and yielded a methylic salt which, after crystallisation from alcohol, melted at  $79\text{--}80^\circ$ ; this was identical with the substance of the same melting point described on page 177 as methylic methylisophthalate.

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MANCHESTER.

# SYNTHESIS OF *i*-CAMPHORONIC ACID.

BY

WILLIAM HENRY PERKIN, JUN.,

AND

JOCELYN FIELD THORPE.

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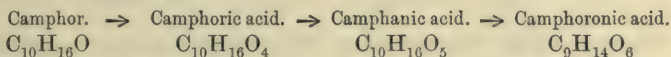
From the Transactions of the Chemical Society, 1897.



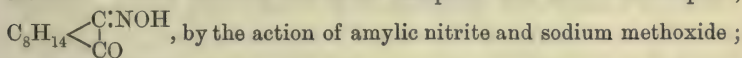
## Synthesis of *i*-Camphoronic Acid.

By WILLIAM HENRY PERKIN, jun., and JOCELYN FIELD THORPE.

AMONG the reactions which, up to the present, have thrown light on the constitution of camphor, its oxidation by means of nitric acid has probably yielded by far the most valuable results. Laurent (*Annalen*, 1837, 22, 135) first showed that camphoric acid was formed during this process, and Kachler (*Annalen*, 1871, 159, 302) first isolated camphoronic acid from the products of the oxidation; subsequently, Roser (*Ber.*, 1885, 18, 3112) obtained camphanic acid (hydroxy-camphoric acid) from the mother liquors which remain when the camphoric and camphoronic acids have been separated. Since camphoric acid may be converted into camphanic acid by careful oxidation (Balbiano, *Rend. Acc. Lincei*, 1893, ii, 240), whilst camphanic acid itself, by treatment with nitric acid or chromic acid, yields considerable quantities of camphoronic acid (Bredt, *Ber.*, 1835, 18, 2989; Koenigs, *Ber.*, 1893, 26, 2337), it is evident that these three acids represent, as Bredt has pointed out, distinct stages in the decomposition of the camphor molecule; the oxidation of camphor may consequently be represented thus:

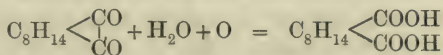


Camphoric acid has been obtained from camphor by Claisen and Manasse (*Annalen*, 274, 86) by a second very interesting method. These chemists converted camphor into isonitrosocamphor,

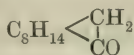


by subsequently treating this substance with nitrous acid, they discovered camphorquinone,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array}$ , an interesting substance

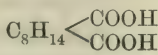
which, when digested with a solution of potash in methylic alcohol, is slowly oxidised (probably by the oxygen of the air) to camphoric acid,



This series of reactions indicates that camphoric acid is very closely related to camphor, and, indeed, it is usually supposed that the former is derived from the latter by the oxidation of the group  $-\text{CH}_2\cdot\text{CO}-$  to two carboxyl groups, the relationship being well understood from the formulæ



Camphor.



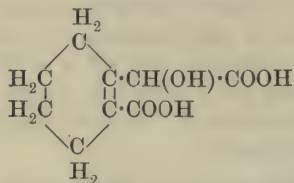
Camphoric acid.



Many experiments have been made with the object of determining the constitution of camphoric acid, and many formulæ have been suggested for this substance ; but it is hardly likely that its constitution will be definitely established until the acid has been prepared synthetically.

In the meantime, chemists have also been busily engaged in endeavouring to discover the constitution of camphoronic acid, as, if the constitution of this acid, which contains only one carbon atom less than camphoric acid, could be definitely settled, very important deductions could obviously be made with regard to the constitution of camphoric acid, and of camphor itself.

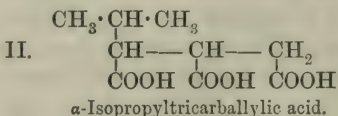
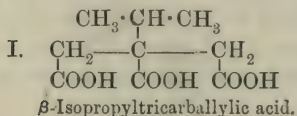
Kachler (*Annalen*, 1873, 169, 185), who first obtained camphoronic acid in a pure state, considered the acid to be a hydroxydibasic acid,  $C_9H_{12}O_5$ , crystallising with  $1H_2O$ , and he suggested the following formula as best expressing its constitution :



Kissling (*Inaug. Diss. Würzburg*, 1878) first showed that camphoronic acid had the formula  $C_9H_{14}O_6$ , and both he and Reyher (*Inaug. Diss. Leipzig*, 1891) considered the acid to be a hydroxyketodicarboxylic acid of the formula  $CH(CH_3)_2 \cdot CH(COOH) \cdot CO \cdot CH_2 \cdot CH(OH) \cdot COOH$ .

Bredt (*Annalen*, 1884, 226, 249—261) it was who, as the result of a careful investigation of the salts of camphoronic acid, first clearly showed that the acid was tribasic ; and further, as the acid distilled under diminished pressure without decomposing, he concluded that the three carboxyl groups must be attached to three different carbon atoms, otherwise, if any two carboxyl groups were attached to the same carbon atom, the acid would be a substituted malonic acid, and like this acid lose carbon dioxide at high temperatures.

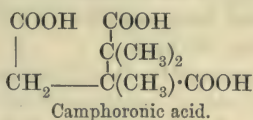
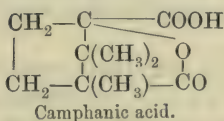
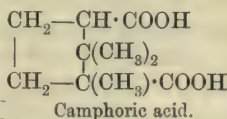
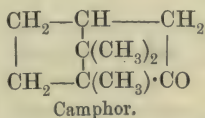
Bredt, at that time, thought it possible that the constitution of camphoronic acid was represented by one of the following formulæ, of which he considered I the more probable :



Subsequently, Collie (*Ber.*, 1892, 25, 1116) arrived at the second formula for camphoronic acid, from the consideration of a new constitution for

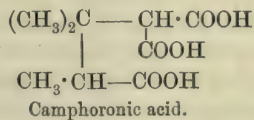
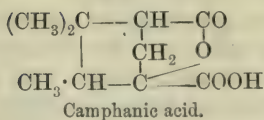
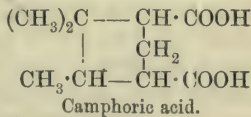
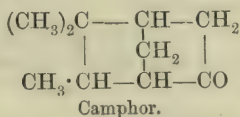
camphor which he had suggested, but this formula was clearly proved to be incorrect by Kölner and von Meyenburg (*Ber.*, 1891, **24**, 2899), who prepared  $\alpha$ -isopropyltricarballic acid synthetically, and showed that its properties were quite different from those of camphoronic acid.

The next important step, which had a direct bearing on the question of the constitution of camphoronic acid, was the discovery by Brecht and Helle (*Ber.*, 1885, **18**, 2990; 1893, **26**, 3049) that this acid, when distilled under the ordinary pressure, is slowly but almost completely decomposed with formation of trimethylsuccinic acid, isobutyric acid, and other products. Since the formation of trimethylsuccinic acid in this way is an indication that camphoronic acid probably contains the group  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \overset{\cdot}{\text{C}}(\text{CH}_3) \cdot \text{COOH}$ , Brecht proposed the formula  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3)(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$  for camphoronic acid, and represented the series—camphor, camphoric acid, camphanic acid, and camphoronic acid—in the following way:



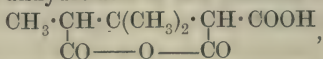
bringing out very clearly the relationship which exists between them.

Recently Tiemann (*Ber.*, 1895, **28**, 1089) suggested a modification of Brecht's formula as the probable constitution of camphor, and was thus led to represent the above series in quite a different way.



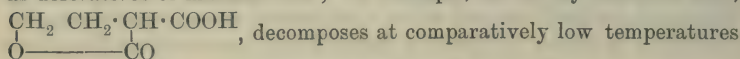
It is remarkable that Tiemann should have suggested a formula for camphoronic acid which contains the group  $-\text{CH}(\text{COOH})_2$ , especially when it is borne in mind that this acid may be distilled without loss of carbon dioxide at  $200^\circ$  under reduced pressure, a behaviour which is shown by no other derivative of malonic acid. In order to get over

this difficulty, Tiemann assumes that camphoronic acid, when heated, is converted into an anhydro-acid of the formula



and that this acid is stable at high temperatures.

But, as was pointed out by one of us (*Proc.*, 1896, p. 189), compounds of this nature when heated lose carbon dioxide in the same way as derivatives of malonic acid; for example, carbobutyrolactonic acid,



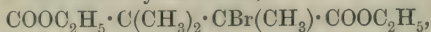
decomposes at comparatively low temperatures quite readily into butyrolactone and carbon dioxide, but a still better example is given by Bredt (*Annalen*, 1896, 292, 130) in ethylmethylcarboxyglutaric acid,  $\text{COOH} \cdot \text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{C}(\text{C}_2\text{H}_5)(\text{COOH})_2$  (Bischoff, *Ber.*, 1891, 24, 1050), the formula of which is closely related to Tiemann's formula for camphoronic acid, and which, when heated at  $166.5^\circ$ , melts with evolution of carbon dioxide.

In order, however, to bring still further evidence against Tiemann's formula camphoronic acid was heated under conditions which precluded the possibility of the formation of the anhydro-acid, namely, in solution in water at  $230^\circ$ , and still no decomposition could be detected, the acid being recovered quite unchanged on evaporating the solution (Perkin, *loc. cit.*).

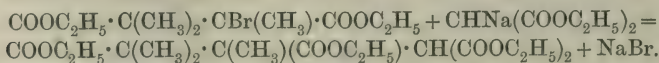
Subsequently, Bredt (*Annalen*, 1896, 292, 131) showed that the tri-ethylic salt of camphoronic acid does not react with sodium, as it would be expected to do if it contained the group  $-\text{CH}(\text{COOC}_2\text{H}_5)_2$ .

Whilst, then, it had been shown that Tiemann's formula was incorrect, it still remained to prove definitely the correctness of Bredt's formula, and the most satisfactory way of doing this seemed to be to prepare an acid of this formula synthetically, and to compare the synthetical acid with that obtained from camphor.

The first experiments on this subject were instituted by Dr. Bone and one of us, and the method which was then tried was the following. Ethylic bromotrimethylsuccinate,

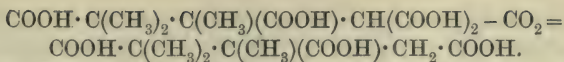


was first prepared by brominating trimethylsuccinic anhydride and treating the bromo-anhydride thus obtained with alcohol. This ethereal salt was then digested in alcoholic solution with ethylic sodiomalonate, when it was expected that the following reaction would take place.



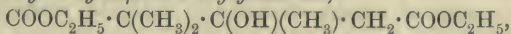
The ethereal salt thus formed should, on hydrolysis and elimination of carbon dioxide, yield camphoronic acid,



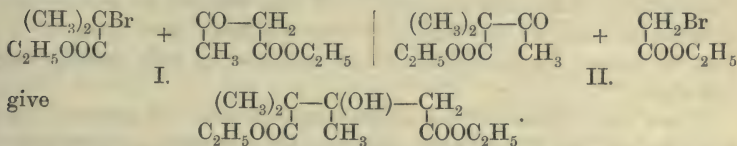


The product of this reaction, after hydrolysis and subsequent heating at 180°, was carefully investigated, but it did not appear to contain camphoronic acid. As, however, we were at that time not sufficiently well acquainted with the method of isolation of small quantities of camphoronic acid, we are again investigating this reaction, and hope soon to be able to communicate the results of our experiments to the Society. Several other reactions which seemed likely to yield camphoronic acid were subsequently investigated, but also without success, until ultimately the method which is described in this paper was devised and found on trial to give the desired result.

*Ethylic β-hydroxy-ααβ-trimethylglutarate,*



was prepared by two different reactions which left no doubt as to its constitution, namely, the action of zinc on mixtures of (I) ethylic acetoacetate with ethylic bromisobutyrate, and (II) ethylic dimethyl-acetoacetate with ethylic bromacetate.\*



In both cases, an ethereal salt boiling at 165° (30 mm.) was obtained; this consisted for the most part of ethylic hydroxytrimethylglutarate, but mixed with varying quantities of ethylic trimethylglutaconate,  $\text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{COOC}_2\text{H}_5$ , the latter being produced by the elimination of water from the hydroxy-compound, either during the condensation, or more probably during the subsequent fractionation of the ethereal salt under reduced pressure. Since, then, the products from the two reactions represented above are identical, there can be no doubt as to the constitution of the compound used as the starting point in this synthesis. When ethylic hydroxytrimethylglutarate, obtained by either of these methods, is hydrolysed with dilute hydrochloric acid, β-hydroxy-ααβ-trimethylglutaric acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{OH})(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOH}$ , melting at 128° is produced, together with small quantities of trimethylglutaconic acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{COOH}$ ; if, however, concentrated hydrochloric acid is employed, the product of the reaction consists almost entirely of the latter acid. Boiling with alcoholic potash decomposes ethylic hydroxytrimethylglutarate with formation of acetic and isobutyric acids.

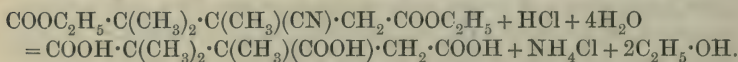
\* Compare Trans., 1896, 69, 1463.



Ethylic hydroxytrimethylglutarate is readily acted on by phosphorus pentachloride with formation of ethylic chlorotrimethylglutarate,  $\text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CCl}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ , boiling at  $139^\circ$  under 20 mm. pressure; this has been obtained in a pure condition only on one or two occasions, as usually it contains varying quantities of ethylic trimethylglutaconate, which, as stated above, is present in the hydroxy-ethereal salt prepared by the methods adopted. Ethylic bromotrimethylglutarate, prepared in an analogous way, boils at  $160^\circ$  (35 mm.). If either the chloro- or bromo-derivative is heated with potassium cyanide and alcohol at  $160^\circ$  for 12 hours, ethylic cyanotrimethylglutarate,  $\text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CN})(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ , is obtained as a colourless oil which distils approximately at  $170$ — $175^\circ$  (25 mm.); this, like the bromo- and chloro-derivatives, always contains varying quantities of ethylic trimethylglutaconate, so much of the latter sometimes being present that it must evidently be produced by the action of the potassium cyanide on the halogen ethereal salt.

When the cyano-ethereal salt is hydrolysed by boiling with hydrochloric acid, and the product allowed to cool, large quantities of trimethylglutaconic acid separate; and the amount is usually so considerable that we are forced to the conclusion that some of it must be formed by the elimination of hydrogen cyanide during the hydrolysis.

If now the crystals of trimethylglutaconic acid are removed by filtration, and the filtrate, after being rendered strongly alkaline with ammonia, is mixed with barium chloride, no precipitate is produced in the cold, but, on boiling, a small quantity of a sparingly soluble barium salt separates; this has been proved to be the barium salt of *i*-camphoronic acid, the synthesis of the acid having taken place thus:



Aschan (*Ber.*, 1895, 28, 16 and 224), who has so carefully examined camphoronic acid, has shown that this acid is capable of existing in three well-defined modifications, namely, as *d*-, *l*-, and *i*-camphoronic acid. *d*-Camphoronic acid,\* produced by the oxidation of *d*-camphor and of *d*-camphoric acid, melts at  $156^\circ$ , dissolves in 6 parts of water at  $20^\circ$ , and is lævorotatory,  $[\alpha]_D = -26.9$ .

*l*-Camphoronic acid, which was isolated by Aschan from the residues

\* As ordinary camphoronic acid is derived from the oxidation of *d*-camphor and *d*-camphoric acid, it appears to us that, although it happens to be lævorotatory, it must nevertheless be called *d*-camphoronic acid; the relationship between these substances being somewhat similar to that of *d*-glucose and *d*-fructose, the latter receiving the prefix *d* in spite of its powerful lævorotatory action, owing to its belonging to the same class as *d*-glucose. For this reason we have taken the liberty of reversing the prefixes *d* and *l* used by Aschan.

obtained in the preparation of *l*-camphoric acid from *l*-borneol, melts at 158—159°, dissolves in 6 parts of water at 20°, and is dextrorotatory, the value  $[\alpha]_D = +27.05$  corresponding exactly with the reverse value of the *d*-acid.

*i*-Camphoronic acid was prepared by Aschan by mixing solutions of equal proportions of the *d*- and *l*-acids; it differs from the active acids in being much less soluble in water (1 part requires 27 parts of water at 20°), in crystallising in much better defined crystals, and in melting at a somewhat higher temperature, namely, about 172°.

Thanks to the kindness of Dr. Aschan in sending us a small sample of his inactive acid, we were enabled to compare its properties with those of the synthetical acid obtained by us, the result proving that the two acids are identical, the following points being perhaps especially worthy of notice.

(1) Both acids crystallise from water in hard, transparent prisms, which, when examined under the microscope, are seen to be identical in form.

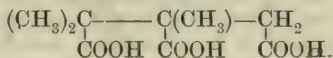
(2) Both acids when heated side by side on the same thermometer soften at about 167° and melt at 169—172°, moreover, no alteration in the melting point could be observed when they were mixed in equal proportions.

(3) A solution of either acid in water, after the addition of excess of ammonia, gives no precipitate with barium chloride in the cold, but on warming a very sparingly soluble barium salt separates, closely resembling barium sulphate in appearance.

(4) When heated with acetic anhydride under the conditions described in the experimental part of this paper, both acids give the same *anhydrocamphoronic acid*, melting at about 136—137°.

(5) An aqueous solution of the synthetical acid was examined by Dr. W. H. Perkin, sen., and found to be inactive.

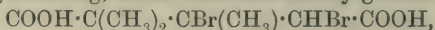
There can be no doubt that the synthetical acid is *i*-camphoronic acid, and this synthesis proves conclusively that camphoronic acid must, as was first suggested by Bredt (*Ber.*, 1893, 26, 3049), have the constitution of a trimethyltricarballic acid of the formula



It is very unfortunate that, for reasons stated above, the yield of camphoronic acid obtained in this synthesis should be small, so small, indeed, as to necessitate the employment of large quantities of material in order to prepare a few grams of the acid. In order to determine whether an independent worker would get the same result as we had done, we requested Mr. Hodgson, a student of Owens College, to repeat from the commencement the whole of our experiments on the synthesis

and isolation of camphoronic acid, and he prepared in the course of his repetition of our work about 2 grams of the pure synthetical acid. We are much indebted to Mr. Hodgson for so kindly placing his time (nearly 4 months) at our disposal, and for the skill with which he carried out this very difficult piece of experimental work.

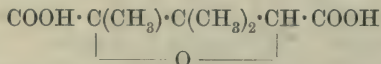
During the course of the above synthetical experiments, a considerable quantity of trimethylglutaconic acid had accumulated, and this we have very carefully investigated, and with very interesting results. Trimethylglutaconic acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{COOH}$ , although unsaturated, is scarcely attacked in the cold by alkaline permanganate, and its solution in chloroform does not decolorise bromine except on long standing, when dibromotrimethylglutaric acid,



melting at  $169^\circ$ , is produced. Sodium amalgam appears to have no action on the solution of the acid in caustic soda even on boiling, and, indeed, great difficulty was experienced in reducing the acid at all; ultimately, however, this was accomplished by repeatedly treating the acid in boiling alcoholic solution with sodium.\*

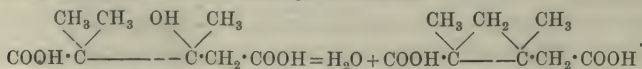
*ααβ-Trimethylglutaric acid*, obtained in this way, is a beautifully crystalline substance which melts at  $112^\circ$  and shows all the properties of a substituted glutaric acid: it is an acid of more than ordinary interest for the following reasons.

In 1894, Balbiano (*Berichte*, 1894, 27, 2133), by the oxidation of camphoric acid with permanganate at the ordinary temperature, obtained a crystalline acid of the formula  $\text{C}_8\text{H}_{12}\text{O}_5$ , the constitution of which, after very careful examination, he now (*Berichte*, 1897, 30, 1908) expresses by the formula



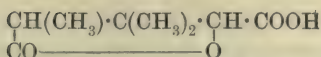
This acid on reduction with hydriodic acid is converted into a monobasic lactone acid of the probable formula

\* This extraordinary stability of trimethylglutaconic acid seems to suggest that there is a possibility of the constitution of the acid being represented by a formula different from that given above. In the elimination of water from hydroxytrimethylglutaric acid or its ethereal salt (or of hydrogen chloride or bromide from the corresponding chloro- or bromo-derivative), it is possible that the change may take place thus with formation of a trimethylene derivative

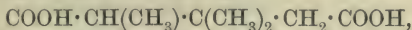


If the acid, called by us trimethylglutaconic acid, should prove to have the constitution represented by the latter formula, it would be easy to understand its stability towards permanganate, bromine, and reducing agents.

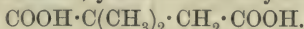




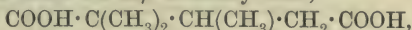
and this, on further reduction, yields a trimethylglutaric acid, which Balbiano assumed to have the formula



since this acid, on oxidation, yields  $\alpha\alpha$ -dimethylsuccinic acid,



This decomposition is no doubt best explained on the assumption that this trimethylglutaric acid has the formula given to it by Balbiano, but on the other hand the  $\alpha\alpha\beta$ -trimethyl acid,

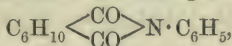


might also yield  $\alpha\alpha$ -dimethylsuccinic acid on oxidation, and therefore, in order to determine the constitution of Balbiano's acid, it was necessary to synthesise either the  $\alpha\alpha\beta$ - or the  $\alpha\beta\beta$ -trimethylglutaric acid, and directly compare the synthetical acid with the acid from camphor.

In view of the great interest attaching to Balbiano's work, we have carefully studied our  $\alpha\alpha\beta$ -trimethylglutaric acid, and we find that, when pure, this acid melts at  $112^\circ$ , that it gives an *anhydride* melting at  $39^\circ$ , and an *anilic acid* melting at  $155^\circ$ . Balbiano's trimethylglutaric acid, on the other hand, melts at  $88\text{--}89^\circ$ , gives an anhydride melting at  $81^\circ$ , and an anilic acid \* melting, not quite sharply, at  $149\text{--}150^\circ$ .

From this, it is evident that Balbiano's acid is isomeric with our  $\alpha\alpha\beta$ -trimethylglutaric acid, and it must therefore be, as its discoverer suggested, the  $\alpha\beta\beta$ -acid,  $\text{COOH} \cdot \text{C}(\text{CH}_3) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

During the course of our experiments on the reduction of trimethylglutaconic acid, we found that this acid, when treated in boiling amyl alcohol solution with sodium is, curiously enough, *not reduced*, but is converted into a most beautifully crystalline substance of the formula  $\text{C}_8\text{H}_{10}\text{O}_3$ . This compound crystallises from water unchanged, but it is, nevertheless, the anhydride of a dibasic acid, since it gives, with aniline, an *anilic acid*,  $\text{C}_6\text{H}_{10}(\text{COOH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  (m. p.  $138^\circ$ ) and this, when heated, is readily converted into the corresponding *anil*,



melting at  $148^\circ$ .

\* This  $\alpha\beta\beta$ -trimethylglutaranilic acid had not been described, and we prepared it for comparison with our isomeric anilic acid by dissolving 0.7 gram of the anhydride of Balbiano's acid in benzene, adding 0.7 gram of aniline and allowing the mixture, which became very warm, to stand. The crystals which separated were collected, recrystallised from dilute methylic alcohol, and the glistening, crystalline mass, which melted approximately at  $149^\circ$ , was analysed with the following result :

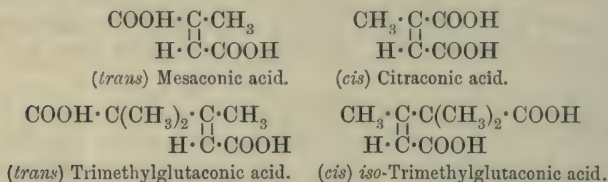
0.1117 gram gave 5.4 c.c. nitrogen at  $17^\circ$  and 760 mm.  $\text{N} = 5.60$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.63$  per cent.



The anhydride, which we have named *iso-trimethylglutaconic anhydride*, dissolves in boiling potash solution, and if the solution be cooled to  $0^{\circ}$  and acidified with hydrochloric acid, the corresponding *iso-trimethylglutaconic acid* is obtained.

At its melting point ( $133^{\circ}$ ), this acid is converted into its anhydride with elimination of water, and the ease with which the anhydride is formed is shown by the fact that if the aqueous solution of the acid boiled, the anhydride, and not the acid, separates on cooling. It seems probable that trimethylglutaconic acid and *iso*-trimethylglutaconic acid like fumaric and maleic acids, or mesaconic and citraconic acids, are stereoisomeric. The similarity in constitution between the two latter acids and the glutaconic acids becomes very clear from an examination of the following formulæ.



The *cis*-modification of trimethylglutaconic acid would, like maleic and citraconic acids, readily yield an anhydride, but it is certainly remarkable that the formation of this anhydride should take place so very easily, the only analogous case being that of xeronic acid (diethylmaleic acid), an acid which is in many respects very similar to *iso*-trimethylglutaconic acid in its properties.

We are at present engaged in a further investigation of the trimethylglutaconic acids with a view of determining whether, and under what conditions, they may be converted into one another.

#### EXPERIMENTAL.

*Condensation of Ethylic Dimethylacetoacetate with Ethylic Bromacetate in the presence of Zinc. Formation of Ethylic  $\alpha\alpha\beta$ -Trimethyl- $\beta$ -hydroxyglutarate,  $\text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{OH})(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ .*

After numerous experiments, it was found that this condensation could best be carried out in the following way.

Ethylac dimethylacetoacetate (50 grams) mixed with ethylac bromacetate (50 grams) is heated in a reflux apparatus on a water bath until the mixture has reached the temperature of  $90$ — $95^{\circ}$ ; a small quantity of zinc\* (about 1 gram) is then added, and the flask shaken

\* In order that this reaction may proceed satisfactorily, the zinc used must be thoroughly cleaned, that is, it must be quite free from grease and oxide; with this object, commercial zinc turnings are first passed through a sieve to remove the

vigorously until the metal has almost dissolved ; another gram of zinc is then added and the process continued until the metal is only very slowly attacked ; excess of zinc is now added and the whole heated on the water bath for 10—12 hours.

The addition of the zinc \* to the hot mixture of ethylic salts in this experiment should be carefully carried out, as otherwise a very violent action may set in, in which case there is a great decrease in the yield owing to overheating and loss of the bromethylic salt by evaporation and decomposition.

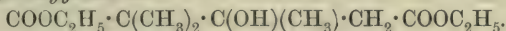
The product consists of a brown, viscous zinc compound containing large quantities of unchanged zinc. On adding dilute sulphuric acid (1 : 10), the zinc compound is decomposed and a brown oil separates which is extracted by three successive treatments with ether, the ethereal solution is washed at least six times with dilute sulphuric acid, then with water, dried over potassium carbonate, and the ether distilled off. It is most important that the ethereal solution should be thoroughly and repeatedly washed with dilute sulphuric acid, as insufficient washing always yields a product containing zinc salts and which decomposes on subsequent distillation. On distilling the oil under reduced pressure (30 mm.), a large quantity of a fraction of low boiling point is first obtained consisting largely of unchanged ethylic dimethylacetoacetate, the thermometer then rises rapidly to 160°, the crude condensation product passing over between this temperature and 180°, leaving a small quantity of substance of high boiling point. On refractionation, the bulk distils at 160—170° (30 mm.). The fraction distilling at 165° (30 mm.) gave the following results on analysis.

0.1420 gave 0.3056 CO<sub>2</sub> and 0.1140 H<sub>2</sub>O. C = 58.69 ; H = 8.92.

0.1278 „ 0.2751 CO<sub>2</sub> and 0.1041 H<sub>2</sub>O. C = 58.60 ; H = 9.05.

C<sub>12</sub>H<sub>22</sub>O<sub>5</sub> requires C = 58.54 ; H = 8.94 per cent.

The substance prepared in this way is a colourless, moderately limpid liquid with a peculiar smell, and consists for the most part of *ethylic trimethylhydroxyglutarate*.

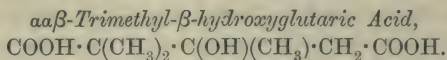


It appears, however (see p. 1173), always to contain some ethylic  $\alpha\beta$ -trimethylglutaconate,  $\text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{COOC}_2\text{H}_5$ ,

coarser particles, and well washed, first with water, then with hot dilute soda, again with water, and lastly with very dilute hydrochloric acid and water. Finally, the zinc is dried by treatment with alcohol and ether, and subsequent heating in a steam oven.

\* In some cases, no action takes place for a long time, the zinc being only very slowly attacked, whilst in others, apparently under exactly the same conditions, the zinc dissolves at once, with considerable rise of temperature. The yield of condensation product is undoubtedly more satisfactory when the reaction proceeds quietly.

produced probably by elimination of water during distillation; sometimes it contains traces only of the unsaturated ethereal salt, whilst at other times large quantities are present.



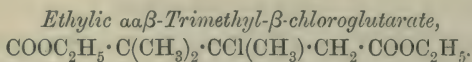
When ethylic trimethylhydroxyglutarate is digested with alcoholic potash, it is entirely split up into acetic and isobutyric acids, but if carefully boiled with dilute hydrochloric acid (3 acid : 1 water) for about 10 to 12 hours, hydrolysis ensues without appreciable decomposition; on cooling, a small quantity of trimethylglutaconic acid,  $\text{COOH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}(\text{CH}_3)\cdot\text{CH}\cdot\text{COOH}$  (p. 1182), separates in the crystalline state.

On allowing the mother liquor from these crystals to evaporate to dryness over potash in a vacuum desiccator, an acid was obtained which, after recrystallisation from a mixture of ethylic acetate and light petroleum, gave the following results on analysis.

0.2134 gave 0.3936  $\text{CO}_2$  and 0.1421  $\text{H}_2\text{O}$ .  $\text{C} = 50.30$  ;  $\text{H} = 7.4$ .

$\text{C}_8\text{H}_{14}\text{O}_5$  requires  $\text{C} = 50.52$  ;  $\text{H} = 7.36$  per cent.

This acid is evidently *trimethylhydroxyglutaric acid*, produced by the direct hydrolysis of the ethereal salt; it crystallises in well-defined, colourless prisms, melts at  $128^\circ$ , and is readily soluble in water and in most solvents except light petroleum



This ethereal salt was prepared by gradually adding phosphorus pentachloride (25 grams) to ethylic trimethylhydroxyglutarate (25 grams) contained in a flask connected with a long tube to lead off the hydrogen chloride produced during the action.

The pentachloride rapidly attacks the oil, and a vigorous reaction takes place with considerable rise of temperature and evolution of much hydrogen chloride; after about an hour, and as soon as the pentachloride has entirely disappeared, the reaction is completed by heating for 15 minutes on the water bath.

The product is now carefully poured into ice cold alcohol, the alcoholic solution, after some time, is mixed with water, the oily deposit extracted with ether, and the ethereal solution well washed with water and dilute sodium carbonate. After drying over calcium chloride and distilling off the ether, crude ethylic trimethylchloroglutarate is obtained as a slightly yellowish oil, which is somewhat unstable, as on distilling it under the ordinary pressure, hydrogen chloride is eliminated



with production of ethylic trimethylglutaconate; under diminished pressure (20 mm.), however, it passes over unchanged at 139° as a colourless oil. On analysis, it yielded the following numbers.

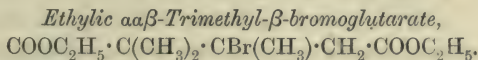
0.2010 gave 0.1935 AgCl. Cl = 13.39.

$C_{12}H_{21}ClO_4$  requires Cl = 13.42 per cent.

The action of phosphorus pentachloride on ethylic trimethylhydroxyglutarate has been carried out in a variety of ways and under various conditions, but only on rare occasions has the product been found to contain the theoretical amount of chlorine as in the case given above.

Frequently the oil has contained only 7—8 per cent. of chlorine, whilst on one occasion it was almost free from halogen, and was found on examination to consist of almost pure ethylic trimethylglutaconate. This unpleasant behaviour, which very much retarded the progress of this research, may be explained by the unsuspected presence of large quantities of ethylic trimethylglutaconate in some of the samples of crude ethylic trimethylhydroxyglutarate used, and also by the elimination of hydrogen chloride from the product of the reaction during distillation, this being due possibly to the presence of moisture and other impurities.

The elimination of hydrogen chloride from ethylic trimethylchloroglutarate undoubtedly takes place very readily; it was found, for example, impossible to reduce it even when ice-cold alcoholic hydrogen chloride and zinc dust were employed as the reducing agent; the temperature was never allowed to rise above 0°, but notwithstanding these precautions the product consisted entirely of ethylic trimethylglutaconate.



This is prepared in a precisely similar manner to the chloro-derivative just described, namely, by the gradual addition of phosphorus pentabromide (52 grams) to ethylic trimethylhydroxyglutarate (25 grams), and subsequently heating the product for a short time on the water bath. It was isolated, exactly as in the case of the chlorinated compound, as a yellowish oil (28 grams) which distilled with slight decomposition at about 145° (18 mm.).

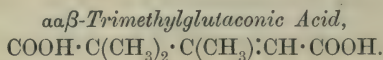
0.2542 gave 0.138 AgBr. Br = 23.12.

$C_{12}H_{21}BrO_4$  requires Br = 25.23 per cent.

The percentage of bromine in the various samples of this bromo-ethereal salt which were prepared during the course of this research varied considerably, although not nearly to the same extent as in the



case of the corresponding chlorinated ethereal salt ; it appears, therefore, that the former is more stable than the latter, and this was borne out by subsequent experiments with these compounds.



During the course of this investigation, this acid has been prepared by a variety of methods, of which the following may be described.

I. *By the Hydrolysis of Ethylic Trimethylhydroxyglutarate.*—It has already been mentioned (p. 1180) that this ethereal salt, when treated with alkalis, does not yield the corresponding acid, but is split up into acetic and isobutyric acids ; if, however, the hydrolysis is carried out by boiling with concentrated hydrochloric acid until the oily ethereal salt has disappeared, the solution on cooling deposits crystals of trimethylglutaconic acid.

After recrystallisation from water, this acid was readily obtained pure, melting at  $148^\circ$ .

0.1663 gave 0.3378  $\text{CO}_2$  and 0.1061  $\text{H}_2\text{O}$ .  $\text{C} = 55.31$  ;  $\text{H} = 7.08$ .

$\text{C}_8\text{H}_{12}\text{O}_4$  requires  $\text{C} = 55.80$  ;  $\text{H} = 6.97$  per cent.

II. *By the Action of Diethylaniline on Ethylic Trimethylbromoglutarate.*—In this experiment, the brominated ethereal salt (23 grams) mixed with diethylaniline (50 grams) was heated to gentle ebullition in a reflux apparatus for about an hour. The dark coloured product, when cold, was mixed with excess of dilute hydrochloric acid, extracted three times with ether, and the ethereal solution, after being well washed with dilute acid, was dried over potassium carbonate and evaporated ; the oily residue, on being submitted to two fractionations under reduced pressure, passed over almost entirely at  $160\text{--}165^\circ$  (30 mm.), and consisted of nearly pure ethylic trimethylglutaconate as the following analysis shows.

0.1390 gave 0.3210  $\text{CO}_2$  and 0.1140  $\text{H}_2\text{O}$ .  $\text{C} = 62.98$  ;  $\text{H} = 9.11$ .

$\text{C}_{12}\text{H}_{20}\text{O}_4$  requires  $\text{C} = 63.16$  ;  $\text{H} = 8.77$  per cent.

The results of the hydrolysis of this ethereal salt with alcoholic potash were not very satisfactory, the acid obtained being contaminated with some sticky substance which rendered it difficult to purify. It is far better to boil it with hydrochloric acid until the oily drops have disappeared ; on cooling, crystals of trimethylglutaconic acid separate and can be readily purified by a single crystallisation from water.

0.1110 gave 0.2279  $\text{CO}_2$  and 0.0710  $\text{H}_2\text{O}$ .  $\text{C} = 55.95$  ;  $\text{H} = 7.10$ .

$\text{C}_8\text{H}_{12}\text{O}_7$  requires  $\text{C} = 55.80$   $\text{H} = 6.97$  per cent.

Alcoholic potash appears to act on ethylic trimethylchloro- or bromoglutarate in somewhat the same way as diethylaniline, since in both cases considerable quantities of trimethylglutaconic acid are formed.

III. *By the Action of Zinc Dust on Ethylic Trimethylchloroglutarate.*—This method, which is a rather curious one to employ in obtaining an unsaturated acid, gives such a good yield of trimethylglutaconic acid that it was usually employed in preparing this substance.

Ethylic trimethylchloroglutarate (25 grams) dissolved in absolute alcohol (100 grams) was saturated with hydrogen chloride, and about 20 grams of zinc dust was then gradually added to the well cooled solution; when all had dissolved, the product was poured into water and extracted three times with ether. The ethereal solution, after being thoroughly washed with water and with dilute sodium carbonate, was dried over anhydrous potassium carbonate, evaporated, and the residual almost colourless oil purified by distillation under reduced pressure (30 mm.); almost the whole passed over between  $160^{\circ}$  and  $165^{\circ}$ , the distillate consisting of nearly pure ethylic trimethylglutaconate containing evidently, at the most, only a trace of ethylic trimethylglutarate.

0.2204 gave 0.5113  $\text{CO}_2$  and 0.1733  $\text{H}_2\text{O}$ .  $\text{C} = 63.27$ ;  $\text{H} = 8.74$ .

$\text{C}_{12}\text{H}_{20}\text{O}_4$  requires  $\text{C} = 63.15$ ;  $\text{H} = 8.77$  per cent.

On hydrolysing this ethereal salt with hydrochloric acid as before, the oily drops disappeared after 12 hours' boiling, and on cooling a large quantity of a crystalline acid slowly separated. This, after being collected and recrystallised from water, was analysed and found to be trimethylglutaconic acid.

0.1510 gave 0.3074  $\text{CO}_2$  and 0.0948  $\text{H}_2\text{O}$ .  $\text{C} = 55.59$ ;  $\text{H} = 6.97$ .

$\text{C}_8\text{H}_{12}\text{O}_4$  requires  $\text{C} = 55.80$ ;  $\text{H} = 6.97$  per cent.

*Trimethylglutaconic acid* is sparingly soluble in cold water, but dissolves readily in boiling water, and separates on cooling in well-defined, lustrous plates which melt at  $148^{\circ}$ . It is remarkable that its solution in sodium carbonate does not decolorise permanganate except on long standing; bromine also acts only very slowly on the acid, with ultimate formation of *trimethyldibromoglutaconic acid*,



(see next section).

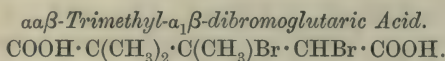
*Salts of Trimethylglutaconic Acid.* The silver salt,  $\text{C}_8\text{H}_{10}\text{Ag}_2\text{O}_4$ .—This is obtained as a white precipitate on adding silver nitrate to a slightly alkaline solution of the ammonium salt.

0.2170, on ignition, gave 0.1211 Ag.  $\text{Ag} = 55.85$ .

$\text{C}_8\text{H}_{10}\text{Ag}_2\text{O}_4$  requires  $\text{Ag} = 55.87$  per cent.

The most characteristic salt of this acid is the *copper salt* which separates from the neutral solution of the ammonium salt on the addition of copper acetate, as a bright blue, crystalline precipitate which is sparingly soluble in water. This salt, which is useful in separating trimethylglutaconic acid from other acids, yields the acid in a beautifully pure condition when decomposed with sulphuretted hydrogen.

Trimethylglutaconic acid dissolves in acetyl chloride, but without formation of an anhydride, the solution, even after boiling for some time, depositing the unchanged acid on evaporation. On the other hand, prolonged boiling with acetic anhydride gives rise to the formation of an oil boiling at about 160—170° (30 mm.) ; this is at present under examination



Bromine acts only very slowly on trimethylglutaconic acid dissolved in chloroform, but on long standing it is gradually absorbed with formation of the dibromo-acid above mentioned. In preparing it, excess of bromine was added to a solution of the unsaturated acid in chloroform and the mixture left for some weeks, during which time a quantity of crystals of the dibromo-compound had separated. The colourless crystals were washed with chloroform and analysed.

0.2901 gave 0.2433 AgBr. Br = 48.10.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Br}_2$  requires Br = 48.19 per cent.

*Trimethyldibromoglutaric acid* melts and decomposes at about 169° ; it is readily soluble in ether, alcohol, acetone, and ethylic acetate, less so in carbon bisulphide and chloroform, and almost insoluble in benzene and light petroleum. It is readily decomposed by boiling with aqueous silver nitrate solution, with separation of silver bromide.

*iso-Trimethylglutaconic Anhydride.*

It has already been stated that trimethylglutaconic acid is only reduced with great difficulty, and in investigating this subject, we on one or two occasions experimented on the action of sodium and boiling amyl alcohol on the acid, and with very remarkable results. The pure unsaturated acid (5 grams) was dissolved in amyl alcohol (600 c.c.), the solution heated to boiling, and then sodium (10 grams) added as rapidly as possible. When all the sodium had dissolved, the product was mixed with water, the amyl alcohol separated, and the aqueous solution boiled until the odour of amyl alcohol was no longer perceptible. The concentrated solution of the sodium salt was then acidified and extracted with ether, when a substance melting at



145°—149° was obtained, which consisted chiefly of the unchanged acid. However, in subsequent experiments where the above process of reduction was repeated five times with the same substance, a product was isolated from the sodium salt which melted at 94—97°, and on recrystallisation from water at 107°. The analysis gave the following results.

0·1081 gave 0·2470 CO<sub>2</sub> and 0·0660 H<sub>2</sub>O. C = 62·31 ; H = 6·79.

0·1201 „ 0·2734 CO<sub>2</sub> „ 0·0738 H<sub>2</sub>O. C = 62·13 ; H = 6·83.

C<sub>8</sub>H<sub>10</sub>O<sub>3</sub> requires C = 62·33 ; H = 6·50 per cent.

This substance, which is an anhydride, and which we propose to name *iso*-trimethylglutaconic anhydride, crystallises from water unchanged ; it is insoluble in dilute solution of sodium carbonate, but dissolves slowly on boiling, and on carefully acidifying the cold solution, it deposits needles of the corresponding acid (see next section). The anhydride crystallises from acetic anhydride unchanged, and separates from a mixture of benzene and light petroleum in magnificent, glistening plates. *iso*-Trimethylglutaconic anhydride was subsequently obtained in considerable quantity in an experiment instituted with the object of preparing ethylic trimethylbromoglutarate (p. 1181), but in which by accident the wrong proportions of the materials were used. Ethylic trimethylhydroxyglutarate (50 grams) was mixed with phosphorus pentabromide (40 grams), and the mixture heated for 6 hours on the water bath ; the product, when cold, was poured into alcohol, without allowing the temperature to rise above 30°, water was then added, and the oily precipitate extracted with ether. After washing the ethereal solution well with water and dilute sodium carbonate solution, and evaporating the ether, a brownish, oily residue was left, the greater part of which distilled between 175° and 185° (35 mm.). The distillate, after being left in an ice chest for a few days, deposited a large quantity of crystals ; these were collected with the aid of the pump and crystallised from benzene and light petroleum. The product consisted of pure *iso*-trimethylglutaconic anhydride melting at 107°.

0·1356 gave 0·3088 CO<sub>2</sub> and 0·0822 H<sub>2</sub>O. C = 62·11 ; H = 6·73.

0·1394 „ 0·3197 CO<sub>2</sub> „ 0·0846 H<sub>2</sub>O. C = 62·60 ; H = 6·73.

C<sub>8</sub>H<sub>10</sub>O<sub>3</sub> requires C = 62·33 ; H = 6·50 per cent.

The oily filtrate from these crystals, on distillation, boiled at 158—165° under a pressure of 25 mm. ; it contained large quantities of bromine, and apparently consisted of ethylic trimethylbromoglutarate.



*iso-Trimethylglutaconanilic Acid*,  $C_{14}H_{17}NO_3 = C_6H_{10} \begin{matrix} \swarrow CO \cdot NH \cdot C_6H_5 \\ \searrow COOH \end{matrix}$

In order to prepare this substance, the pure anhydride was dissolved in benzene and the solution mixed with aniline; very little rise of temperature took place, but on standing for a few days crystals gradually separated. These, when collected and recrystallised from warm dilute methylic alcohol, formed colourless needles.

0.1627 gave 8.2 c.c. nitrogen at  $14^\circ$  and 758 mm.  $N = 5.91$ .

$C_{14}H_{17}NO_3$  requires  $N = 5.67$  per cent.

Trimethylglutaconanilic acid melts at about  $138^\circ$  with rapid decomposition and formation of the corresponding anil.

*iso-Trimethylglutaconanil*,  $C_{14}H_{15}NO_2 = C_6H_{10} \begin{matrix} \swarrow CO \\ \searrow CO \end{matrix} N \cdot C_6H_5$ .

This is readily obtained by heating the anilic acid to boiling for a few minutes and recrystallising the residue from dilute methylic alcohol, when it separates in long, colourless needles melting at  $148^\circ$ .

0.1418 gave 7.2 c.c. nitrogen at  $15^\circ$  and 760 mm.  $N = 5.96$ .

$C_{14}H_{15}NO_2$  requires  $N = 6.11$  per cent.

#### *iso-Trimethylglutaconic Acid.*

This acid could not be prepared by the action of water on the anhydride, as the latter is not acted on by water in the cold, and on boiling, although the anhydride dissolves, it separates again on cooling unchanged. If, however, the anhydride be boiled with excess of aqueous potash, and the solution after cooling to  $0^\circ$  be acidified with dilute hydrochloric acid, the acid will gradually separate as a woolly mass of very fine needles, which, after collecting by means of the pump, washing with ice-cold water, and drying on porous porcelain at the ordinary temperature, gave the following results on analysis.

0.1372 gave 0.2830  $CO_2$  and 0.0916  $H_2O$ .  $C = 56.25$ ;  $H = 7.42$ .

0.1522 „ 0.3117  $CO_2$  „ 0.0996  $H_2O$ .  $C = 55.90$ ;  $H = 7.28$ .

$C_8H_{12}O_4$  requires  $C = 55.81$ ;  $H = 7.00$  per cent.

*iso-Trimethylglutaconic acid* if rapidly heated melts at about  $133^\circ$ , with evolution of aqueous vapour and formation of the anhydride. It is readily soluble in alcohol, ether, or warm water, moderately so in cold water, and although it is possible to recrystallise the acid from water, the aqueous solution must not be boiled, otherwise the anhydride crystallises out on cooling.

*Salts of iso-Trimethylglutaconic Acid.*—The silver salt,  $C_8H_{10}Ag_2O_4$ , separates, on the addition of silver nitrate to the neutral solution of the ammonium salt, as a white, amorphous precipitate which, after washing well, and drying first on a porous plate and then at  $100^\circ$ , gave the following results on analysis.

0.2539 gave, on ignition, 0.1424 Ag. Ag = 56.08.

$C_8H_{10}Ag_2O_4$  requires Ag = 55.87 per cent.

The neutral solution of the ammonium salt shows the following behaviour with reagents.

*Barium chloride* gives at first no precipitate, but after a few minutes a beautifully crystalline barium salt separates in four-sided plates which are very sparingly soluble even in boiling water.

*Calcium chloride* gives at once a microcrystalline precipitate which is very sparingly soluble in boiling water.

*Copper acetate* gives no immediate precipitate even on boiling, but the solution, if left, gradually deposits a beautifully crystalline, copper salt; the crystals under the microscope are deep blue, but not well defined.

*ααβ-Trimethylglutaric Acid*,  $COOH \cdot C(CH_3)_2 \cdot CH(CH_3) \cdot CH_2 \cdot COOH$ .

On account of the interest attaching to the isolation and identification of this acid, which has already been noticed in the introduction to this paper, we made numerous experiments with the object of preparing it from ethylic trimethylhydroxyglutarate, but in performing this apparently simple experiment we met with quite unexpected difficulties. We, in the first place, endeavoured to reduce the hydroxy-ethereal salt directly by heating it with fuming hydriodic acid, and as this failed, we next tried the action of various reducing agents on ethylic trimethylchloroglutarate and on the corresponding bromo-derivative, but in all cases we obtained either trimethylglutaconic acid or uninviting oily products. The results of these experiments seemed to point to the reduction of trimethylglutaconic acid as the only way of preparing trimethylglutaric acid, but it was a long time before a suitable reagent could be found for this purpose.

Sodium amalgam has no action on the unsaturated trimethylglutaconic acid, even when the acid is boiled with a large excess of the amalgam, and heating with hydriodic acid converted the acid into dark coloured, oily substances which could not be purified. Sodium and boiling amyl alcohol gave rise to a very remarkable result, *iso*-trimethylglutaconic anhydride being produced, as explained on p. 1184.

The right reducing agent was, however, at length found in sodium and boiling ethylic alcohol, and the method which we adopted for preparing trimethylglutaric acid was the following.

Five grams of trimethylglutaconic acid was dissolved in 200 c.c. of absolute alcohol and the solution boiled in a reflux apparatus on a sand bath; 20 grams of sodium was then added through the condenser tube as rapidly as possible. When all the sodium had disappeared, the product was dissolved in water, evaporated until free from alcohol, acidified, and the acid extracted several times with ether. The ethereal solution was then evaporated, and the residue reduced again exactly as before. After the whole process had been repeated five times, the acid was extracted with ether, when, on evaporating the solvent, the residue solidified almost completely. The crystalline mass thus obtained melted at 80—95°, and it was found necessary to recrystallise it a great many times from water before the melting point rose to 112°, which appears to be the correct melting point of  $\alpha\alpha\beta$ -trimethylglutaric acid.

0.1280 gave 0.2584 CO<sub>2</sub> and 0.0938 H<sub>2</sub>O. C = 55.08; H = 8.14.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.17; H = 8.05 per cent.

$\alpha\alpha\beta$ -Trimethylglutaric acid, is very readily soluble in water and most organic solvents, but separates readily from its aqueous solution on saturating it with hydrogen chloride.

*Salts of Trimethylglutaric Acid.*—The silver salt, C<sub>8</sub>H<sub>12</sub>Ag<sub>2</sub>O<sub>4</sub>, was obtained in the usual manner as a white, sparingly soluble precipitate, and on analysis, the details of which have unfortunately been lost, gave the correct results.

A neutral solution of the ammonium salt shows the following behaviour with reagents.

*Lead acetate* produces no precipitate in the cold, but, on boiling, a characteristic, heavy, white precipitate separates.

*Mercuric chloride* gives no precipitate with cold moderate dilute solutions, but, on warming, a heavy, yellowish-white, insoluble salt separates.

*Mercurous nitrate* gives, at once, a heavy white precipitate, which dissolves on warming, and separates again as the solution cools.

*Anhydride of  $\alpha\alpha\beta$ -Trimethylglutaric Acid*, CH<sub>3</sub>·CH<math display="block">\begin{array}{c} \text{CH}\_2 \text{---} \text{CO} \\ \text{CH}(\text{CH}\_3)\_2 \cdot \text{CO} \end{array}\text{>O}.

This anhydride was prepared by heating the acid to boiling for some time and then distilling the product. The distillate was dissolved in ether, the ethereal solution rapidly shaken with sodium carbonate solution, dried over calcium chloride and evaporated, when the residue, kept overnight in an ice-chest, solidified completely; this anhydride, purified by recrystallisation from light petroleum, was obtained in fine, colourless prisms; it melts at 39°, and dissolves in boiling water with re-formation of trimethylglutaric acid.



0.2107 gave 0.4774 CO<sub>2</sub> and 0.1443 H<sub>2</sub>O. C = 61.78 ; H = 7.61.

C<sub>8</sub>H<sub>12</sub>O<sub>3</sub> requires C = 61.53 ; H = 7.62 per cent.

*ααβ-Trimethylglutaranilic Acid.*

C<sub>14</sub>H<sub>19</sub>NO<sub>3</sub> = C<sub>6</sub>H<sub>5</sub>·NH·CO·C(CH<sub>3</sub>)<sub>2</sub>·CH(CH<sub>3</sub>)·CH<sub>2</sub>·COOH (?).

On adding aniline to a solution of trimethylglutaric anhydride in pure benzene, a crystalline precipitate of the anilic acid is at once produced. This, after being washed with a little benzene and purified by recrystallisation from dilute alcohol, was obtained in lustrous plates melting at 155°.

0.2060 gave 10 c.c. N<sub>2</sub> at 18° and 773 mm. N = 5.70.

C<sub>14</sub>H<sub>19</sub>NO<sub>3</sub> requires N = 5.63 per cent.

Trimethylglutaranilic acid is readily soluble in most organic solvents, and its general behaviour corresponds closely with that of other known anilic acids of the glutaric series. It dissolves in sodium carbonate solution, but when heated, it does not readily yield the corresponding anil, in fact, small quantities of the anilic acid, if rapidly heated, distil almost without decomposition. On hydrolysis, the anilic acid is decomposed with some difficulty into aniline and trimethylglutaric acid.

*Ethylic ααβ-Trimethyl-β-cyanoglutarate,*

COOC<sub>2</sub>H<sub>5</sub>·C(CH<sub>3</sub>)<sub>2</sub>·C(CN)(CH<sub>3</sub>)·CH<sub>2</sub>·COOC<sub>2</sub>H<sub>5</sub>.

The preparation of this substance and its subsequent conversion into *i*-camphoronic acid were found to be problems of such experimental difficulty as to necessitate more than a year's work before the desired result could be accomplished.

In the first series of experiments, ethylic trimethyl-β-chloroglutarate (p. 1180) was treated with pure potassium cyanide, with or without alcohol and other solvents, at temperatures up to 100°, but even when the constituents had been heated together for 12 hours at that temperature the product was found to contain only traces of nitrogen.

A similar result was obtained when the corresponding bromo-derivative was substituted for the chlorinated compound in the same series of experiments, and a variety of experiments in which very carefully purified, neutral, double cyanides, such as KCN, AgCN ; 2KCN, Zn(CN)<sub>2</sub> ; 2KCN, Hg(CN)<sub>2</sub>, were used instead of the slightly alkaline potassium cyanide, also gave negative results.

Ultimately, however, the desired cyanide was obtained in the following comparatively simple manner.

Ethylic-ααβ-trimethyl-β-chloroglutarate (22 grams) was heated in a sealed tube with pure potassium cyanide (10 grams) and a little alcohol for 6 hours at 150—160°. The dark-coloured product was mixed with



water, extracted with ether, and the ethereal solution, after separation from a considerable quantity of dark brown insoluble matter, was dried over calcium chloride, filtered, and the ether distilled off. In this way, a brown oil was obtained which distilled for the most part at 170—180° (30 mm.), and gave the following result on analysis.

0.1850 gave 6.3 c.c. nitrogen at 15° and 760 mm.  $N = 4.02$ .

$C_{13}H_{21}NO_4$  requires  $N = 5.48$  per cent.

This oil contained, therefore, about 73 per cent. of ethylic cyano-trimethylglutarate, but the percentage of nitrogen was found to vary very considerably in different preparations. This is, of course, due, in the first place, to the fact, already noticed on p. 1181, that the ethylic trimethylchloroglutarate employed always contains some, and often a considerable quantity of, ethylic trimethylglutaconate; it is also due, in a less degree, to the fact that, during the heating with potassium cyanide, a certain amount of the chlorinated ethereal salt appears to be converted into ethylic trimethylglutaconate by elimination of hydrogen chloride. Unfortunately, the boiling points of the cyano-compound, and of the ethylic trimethylglutaconate lie so close together, that separation cannot be effected by fractional distillation; but the presence of the unsaturated ethereal salt is of no great importance in the synthesis for which the cyano-compound was employed.

*Synthesis of i-Camphoronic Acid* ( $\alpha\beta$ -Trimethyltricarballic Acid),  
 $COOH \cdot C(CH_3)_2 \cdot C(CH_3)(COOH) \cdot CH_2 \cdot COOH$ .

When the mixture of ethylic trimethylcyanoglutarate and ethylic-trimethylglutaconate, obtained as described in the previous section, is digested in a reflux apparatus with concentrated hydrochloric acid, it is gradually hydrolysed, and after about 16 hours the oily layer disappears almost entirely. If now the liquid be allowed to stand in an ice chest for 24 hours, practically the whole of the trimethylglutaconic acid present crystallises out, which is fortunate, since the presence of this acid greatly interferes with the isolation of the camphoronic acid. The filtrate from these crystals, which contains the camphoronic acid, is made distinctly alkaline with ammonia, cooled, mixed with an excess of a strong solution of barium chloride, and filtered from any slight precipitate which may have formed. If, now, the filtrate be heated on a water bath and subsequently to boiling, the whole of the camphoronic acid is precipitated in the form of an exceedingly sparingly soluble barium salt. This salt is collected by means of the pump, well washed, and decomposed with the calculated quantity of dilute sulphuric acid; the filtrate from the barium sulphate, if concentrated and allowed to stand in an ice-chest, deposits beautiful, colourless, transparent prisms

melting at about 158—160°; after recrystallisation, however, the melting point rose to about 168°,\* decomposition occurring at the same time. The results of the analysis agree with those required by camphoronic acid.

0.1258 gave 0.2276 CO<sub>2</sub> and 0.0746 H<sub>2</sub>O. C = 49.34; H = 6.58.

0.1294 „ 0.2348 CO<sub>2</sub> „ 0.0766 H<sub>2</sub>O. C = 49.38; H = 6.57.

C<sub>9</sub>H<sub>14</sub>O<sub>6</sub> requires C = 49.50; H = 6.40 per cent.

This acid is much less soluble in water than ordinary *d*-camphoronic acid, and crystallises in much more definite crystals; it was further characterised by converting it into the following derivatives, which were carefully compared with the corresponding derivatives obtained from a small quantity of *i*-camphoronic acid which Dr. O. Aschan kindly sent us, and which had been prepared by crystallising together equal quantities of the *d*- and *l*-acids.

*i*-Anhydrocamphoronic Acid, C<sub>9</sub>H<sub>12</sub>O<sub>5</sub>.—As the result of experiments with *d*-camphoronic acid, it was found that, in cases like the present, where only very small quantities of substance are available, the conversion of camphoronic acid into the corresponding anhydro-acid is best accomplished as follows.

The finely powdered substance is boiled, in a reflux apparatus, with a large excess of acetyl chloride until it has entirely dissolved, which is usually the case in about half an hour, the acetyl chloride is then evaporated off on the water bath, and the residue allowed to remain over solid potash in a vacuum desiccator until it has completely solidified. The product is then dissolved in a small quantity of boiling benzene, which had previously been carefully dried by repeated distillation over sodium, and the solution allowed to stand overnight. The crystals of the anhydro-acid which separate are collected, washed with a little benzene, and dried at 100°.

The anhydro-acid obtained from synthetical *i*-camphoronic acid in this way began to soften slightly at 128—130°, and melted suddenly at 136—137°.†

0.1284 gave 0.2544 CO<sub>2</sub> and 0.0706 H<sub>2</sub>O. C = 54.03; H = 6.11.

C<sub>9</sub>H<sub>12</sub>O<sub>5</sub> requires C = 54.00; H = 6.00 per cent.

The anhydro-acid, prepared from Aschan's *i*-camphoronic acid under the same conditions, could not be distinguished from the synthetical substance, and as the former has not previously been described, it was also analysed.

\* The melting point of camphoronic acid depends very much on the conditions observed during the determination; this has also been noticed by Aschan.

† It is not improbable that this melting point may be somewhat too low, but the amount of substance at our disposal was so small that we could not subject it to further crystallisation.

0.1322 gave 0.2610  $\text{CO}_2$  and 0.0718  $\text{H}_2\text{O}$ .  $\text{C} = 53.84$ ;  $\text{H} = 6.03$ .

$\text{C}_9\text{H}_{12}\text{O}_5$  requires  $\text{C} = 54.00$ ;  $\text{H} = 6.00$  per cent.

*i*-Camphoronanilic acid,  $\text{C}_{15}\text{H}_{19}\text{NO}_5$ .\*—This was obtained by treating anhydrocamphoronic acid with aniline, parallel experiments being made both with our synthetical acid and with Aschan's acid, the conditions observed being exactly the same in both cases. The anhydro-acid was dissolved in hot benzene in a test-tube, the bulk of the benzene was then boiled away, and the cold, supersaturated solution mixed with rather more than the requisite quantity of aniline. The clear solution becomes warm, then suddenly turbid, and deposits either a mass of colourless crystals or an oil which rapidly solidifies on rubbing with a glass rod. The crystals were washed with benzene, drained on a porous plate, and dried at  $100^\circ$ , they then melted at about  $140^\circ$ . This substance is not very easy to purify by recrystallisation, but if it is dissolved in a little hot alcohol, and the solution is then mixed with about three times its bulk of benzene, the anilic acid gradually separates in colourless crystals which melt at about  $149^\circ$  with decomposition.

The anilic acid prepared from synthetical *i*-camphoronic acid gave the following results on analysis.

0.0580 gave 2.44 c.c. nitrogen at  $16^\circ$  and 762 mm.  $\text{N} = 4.85$ .

$\text{C}_{15}\text{H}_{19}\text{NO}_5$  requires  $\text{N} = 4.77$ .

*i*-Camphoronanilic acid, prepared from Aschan's *i*-camphoronic acid, had the same melting point and properties as the synthetical substance.

0.1022 gave 4.4 c.c. nitrogen at  $20^\circ \text{C}$ . and 754 mm.  $\text{N} = 4.88$ .

$\text{C}_{15}\text{H}_{19}\text{NO}_5$  requires  $\text{N} = 4.77$  per cent.

*Condensation of Ethylic Acetoacetate with Ethylic  $\alpha$ -Bromisobutyrate in presence of Zinc. Second Synthesis of Ethylic  $\alpha\alpha\beta$ -Trimethylhydroxyglutarate,  $\text{COOC}_2\text{H}_5 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{OH})(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ .*

As already stated in the introduction, this condensation was investigated in order to prove the constitution of the ethylic trimethylhydroxyglutarate used in this research. The experiment was carried out in a manner precisely similar to that with ethylic dimethylaceto-

\* *d*-Camphoronanilic acid.—In order to determine the conditions for preparing the anilic acid from *i*-camphoronic acid, experiments were, in the first place, made with the *d*-acid, and by using the above method considerable quantities of *d*-camphoronanilic acid were prepared. This compound, which has not been previously described, melts, after recrystallisation, at  $147$ – $148^\circ$ , and closely resembles the *i*-modification in its properties.

0.112 gave 5 c.c. nitrogen at  $24^\circ$  and 754 mm.  $\text{N} = 5.00$ ,

$\text{C}_{15}\text{H}_{19}\text{NO}_5$  requires  $\text{N} = 4.77$  per cent,



acetate and ethylic bromacetate already described. The bromo-ether (84 grams) was mixed with ethylic dimethylacetoacetate (58 grams), and the zinc gradually added to the hot mixture, the same precautions being observed as in the previous case, great care being taken to prevent the temperature rising too high, as, unless this is done, a most violent action sets in and the yield of product is then very small. The product, treated exactly as described on p. 1179, gave an oil boiling at 160—170° (30 mm.).

0.1775 gave 0.3828  $\text{CO}_2$  and 0.1722  $\text{H}_2\text{O}$ .  $\text{C} = 58.82$ ;  $\text{H} = 8.90$ .

$\text{C}_{12}\text{H}_{22}\text{O}_5$  requires  $\text{C} = 58.53$ ;  $\text{H} = 8.94$  per cent.

As will be shown below, this ethereal salt is identical with the condensation product obtained by the action of zinc on a mixture of ethylic dimethylacetoacetate and ethylic bromacetate, and both products, therefore, must consist of ethylic  $\alpha\alpha\beta$ -trimethyl- $\beta$ -hydroxyglutarate. The yield obtained with the bromacetate is as much as 20—25 per cent. of the theoretical, whilst if ethylic bromisobutyrate is employed the yield hardly ever rises above 8—10 per cent. of the theoretical.

This appears to be due to the fact that zinc acts more readily on ethylic bromisobutyrate than on ethylic bromacetate, and when the former is employed large quantities of product of low boiling point are obtained. These oils, on refractionation under the ordinary pressure, were readily separated into two fractions, namely, a very large one, 110—125°, consisting of a mixture of ethylic isobutyrate and ethylic methylacrylate,  $\text{CH}_2\text{C}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$ , and a fraction, 170—185°, consisting of unchanged ethylic acetoacetate.

Experiments were now made with the object of proving that the compound produced by the condensation of ethylic acetoacetate and ethylic bromisobutyrate is identical with that obtained by the condensation of ethylic dimethylacetoacetate with ethylic bromacetate, and in order to do this the same derivatives were prepared from the former product as have already been described as resulting from the latter. When treated with phosphorus pentachloride or pentabromide, the condensation product from ethylic bromisobutyrate yielded halogen derivatives identical in boiling point and other properties with those described on pp. 1180 and 1181.

Both the chloro- and the bromo-derivative, on treatment with zinc and subsequent hydrolysis (see p. 1183), yielded trimethylglutaconic acid melting at 148°. On analysis, this gave the following result.

0.2091 gave 0.4265  $\text{CO}_2$  and 0.1302  $\text{H}_2\text{O}$ .  $\text{C} = 55.63$ ;  $\text{H} = 6.92$ .

$\text{C}_8\text{H}_{12}\text{O}_4$  requires  $\text{C} = 55.81$ ;  $\text{H} = 6.97$  per cent.

From this acid, on reduction with sodium and alcohol,  $\alpha\alpha\beta$ -trimethyl-



glutaric acid (m. p.  $112^{\circ}$ ) was prepared, and its identity proved by analysis and by converting it into its anhydride (m. p.  $39^{\circ}$ ) and into its anilic acid (m. p.  $155^{\circ}$ ).

These experiments prove conclusively the identity of the two condensation products.

In preparing large quantities of the condensation product from ethylic bromisobutyrate and ethylic acetoacetate, we found it convenient to distil off the oil of low boiling point formed during the condensation, and to reserve the residue until a considerable quantity had accumulated, before purifying it by fractionation. On standing, this crude product deposited a small quantity of a solid substance; this was collected, washed with ether to free it from oil, and the sparingly soluble crystals were recrystallised from boiling alcohol. The substance was thus obtained in the form of magnificent, long needles, closely resembling asbestos in appearance, but the quantity at our disposal was so small that only one analysis could be carried out, and this gave us no clue as to its constitution.

0.1214 gave 0.2768  $\text{CO}_2$  and 0.0588  $\text{H}_2\text{O}$ .  $\text{C} = 62.28$ ;  $\text{H} = 5.38$ .

$\text{C}_{10}\text{H}_{10}\text{O}_4$  requires  $\text{C} = 61.85$ ;  $\text{H} = 5.15$  per cent.

This substance melts at  $169^{\circ}$  and dissolves in soda, forming a bright yellow solution, the colour of which disappears on boiling; on acidifying the colourless solution with hydrochloric acid, it deposits an oil. It is nearly insoluble in ether, but dissolves readily in alcohol, especially on warming, and the solution gives an intense violet coloration with ferric chloride.

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DECOMPOSITION OF CAMPHORIC ACID BY FUSION  
WITH POTASH OR SODA.

BY

ARTHUR WILLIAM CROSSLEY

AND

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From the Transactions of the Chemical Society, 1898





## Decomposition of Camphoric Acid by Fusion with Potash or Soda.

By ARTHUR WILLIAM CROSSLEY and WILLIAM HENRY PERKIN, JUNR.

IN experimenting on the constitution of camphoric acid, one of the most characteristic properties which at once presents itself is the great stability of the acid, a property which makes it very difficult to attack by reagents and thus resolve it into smaller molecules.

It occurred to us, at an early stage in our experiments, that this difficulty might possibly be got over by the introduction of hydroxy-groups, as it seemed probable that a hydroxycamphoric acid would be more readily attacked than camphoric acid itself.

Some experiments which support this view have already been published by Rudzinski-Rudno (*Inaugural Dissertation Wurzburg*, 1879), who succeeded in oxidising hydroxycamphoric acid (camphanic acid) by means of potassium dichromate and sulphuric acid, the product being an acid to which he assigned the composition  $C_6H_{10}O_4$ , but this, as was afterwards shown by Bredt (*Annalen*, 145, 212), was in reality camphoronic acid. There can be no doubt that, under these conditions, camphanic acid is much more readily oxidised than camphoric acid.

Besides camphanic acid there has been another hydroxycamphoric acid described, namely, the so-called  $\alpha$ -hydroxycamphoric acid, which Hlasiwetz and Grabowski (*Annalen*, 1868, 145, 212) claim to have obtained by fusing camphoric acid with potash. It seemed probable to us that this acid, which is described as a thick syrup, and has therefore properties quite different from those of the beautifully crystalline camphanic acid, might yield important clues to the con-

stitution of camphoric acid if its behaviour towards reagents, and more especially to oxidising agents, was carefully studied and the results compared with those obtained with the isomeric camphanic acid. We therefore decided to prepare and examine this acid, and with this object carefully repeated the experiments of Hlasiwetz and Grabowski, without, however, being able to isolate even traces of an acid of the composition of a hydroxycamphoric acid.

Hlasiwetz and Grabowski fused 15 grams of camphoric acid with 45 grams of potash in a silver dish, acidified and extracted the product with ether; the residue, after distilling off the ether, was then distilled in steam to drive over the volatile fatty acids present. The distillate (which we now know to contain at least 10 different acids), was neutralised with ammonia, and the silver salt prepared and crystallised from water; on analysing this silver salt, numbers were obtained which led these chemists to the conclusion that the silver salt was silver butyrate or a mixture of this salt with silver isovalerate.

The acids which were not volatile with steam were dissolved in ammonia, the solution boiled with calcium chloride, and the insoluble precipitate, which consisted of calcium pimelate,\* removed by filtration; the filtrate from this salt was decomposed by dilute sulphuric acid, filtered from calcium sulphate, the filtrate decolorised with animal charcoal, and extracted with ether. On distilling off the ether, a syrup was left which was dissolved in water and precipitated by lead acetate; the caseous lead salt was then decomposed with hydrogen sulphide, and the syrupy mass obtained gave, on analysis, numbers which, as these authors state, did not agree very well together, but nevertheless pointed to the formula  $C_{10}H_{16}O_5$ , that of a hydroxycamphoric acid. This acid was not altered by fusion with potash, but on distillation it gave a small quantity of camphoric acid, and we have no doubt that it was a mixture of several substances.

During the course of numerous preliminary experiments on the fusion of camphoric acid with potash, we found that the decomposition was much more complex than Hlasiwetz and Grabowski supposed, and as there was every prospect that the careful and systematic examination of the substances formed might give some clue to the constitution of camphoric acid, we decided to devote our attention to the study of this reaction.

Our first experiments were made with the quantities and under the conditions recommended by Hlasiwetz and Grabowski, but subsequently we found that the same results were obtained whether we fused 25, 50, or 100 grams of camphoric acid in one operation, and after having fused in this way about 2 kilos. of camphoric acid, we devoted some

\* The "pimelic acid" referred to repeatedly in this research is always isopropylsuccinic acid,  $CH(CH_3)_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$ .

months to the investigation of the products which had been formed. However, as the work progressed, and we gradually became thoroughly aware of the complicated nature of the mixture of substances with which we had to deal, it was at once evident that the investigation could not be satisfactorily carried out unless very large quantities of material were employed.

But then serious difficulties presented themselves, for the ordinary laboratory apparatus would not permit of sufficiently large quantities being handled conveniently; ultimately, however, through the great kindness of Mr. Ivan Levinstein, these obstacles were overcome, and we were enabled to fuse as much as 500 grams of camphoric acid in one operation. Mr. Levinstein placed a large room in his works at Crumpsall, near Manchester, at our entire disposal, and after having consulted with us, fitted up all the special apparatus which was necessary for carrying out our experiments on the large scale. We beg to take this opportunity of thanking Mr. Levinstein for his great kindness and liberality, without which it would have been impossible to have carried out this work, and we also thank him for the interest which he took in the subsequent progress of our research.

In our preliminary investigations, we had found that when caustic soda was used instead of caustic potash, the nature of the products of decomposition seemed to be in many respects different; it was therefore thought advisable to try the fusion of camphoric acid with caustic soda on the large scale, and the subsequent results show that this decision was thoroughly warranted.

#### *I.—The Substances Formed when Camphoric Acid is Fused with Potash.*

The method adopted in carrying out the fusion is described in detail in the experimental part of this paper, and we therefore propose only to give here a brief account of the way the melts were worked up and the nature of the products obtained.

The melts from 5 kilos. of camphoric acid were dissolved in water, acidified, and distilled with steam until the condensed water had only the faintest acid reaction; the distillate was neutralised, evaporated down to a small bulk, acidified, and extracted with ether, when about 2.3 kilos. of oily fatty acids were obtained.

The residue in the still was filtered from the potassium sulphate which crystallised out on cooling, neutralised with caustic soda, and evaporated, when the concentrated liquor, on standing, deposited a large quantity of the sulphates of sodium and potassium mixed with a considerable amount of organic salts. These crystals were collected, dissolved in water, acidified, and extracted with ether, and in this way 510 grams of a pale yellow oil (A) was obtained. From the mother



liquor from the crystals, 346 grams of a dark yellow oil (B) was subsequently extracted.

The 2·3 kilos. of fatty acids were submitted to most careful fractional distillation in specially constructed apparatus, and ultimately the following acids were isolated and identified, not only by the boiling points and analysis of the acids themselves and of their silver salts, but also by the preparation of their anilides, and in some cases of their paratoluidides.

Name.	Formula.	Boiling point.*
Acetic acid.....	$\text{CH}_3\cdot\text{COOH}$	118°
Propionic acid .....	$\text{CH}_3\cdot\text{CH}_2\cdot\text{COOH}$	141
Isobutyric acid .....	$\text{CH}(\text{CH}_3)_2\cdot\text{COOH}$	154
Isovaleric acid .....	$\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOH}$	174
Methylisopropylacetic acid .....	$\text{CH}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$	190

In view of the fact that it is now generally assumed that camphoric acid contains the group  $(\text{CH}_3)_2\text{C}\cdot\text{C}(\text{CH}_3)-$ , it is interesting to note the repeated occurrence of the isopropyl group,  $(\text{CH}_3)_2\text{CH}-$ , in the above acids, and of the whole group,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{CH}_3)-$ , in the last acid in the table.

The acids distilling above 190° were very difficult to work with, but by converting the portion boiling at 206—212° into the mixed anilides, and crystallising these from light petroleum, a very sparingly soluble, well characterised anilide was obtained which melted at 105°, and on analysis gave numbers agreeing with the formula  $\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ . The acid obtained by the hydrolysis of this pure anilide, boiled constantly at 209—210°, and had the composition  $\text{C}_6\text{H}_{13}\cdot\text{COOH}$ , but, apparently, it is not identical with any of the acids of this formula which have hitherto been investigated. Without having any definite proof to offer, we think it likely that this acid may be *βββ-dimethyl-ethylpropionic acid*,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{COOH}$ , and we are endeavouring to prepare this acid synthetically with the view of deciding this point.

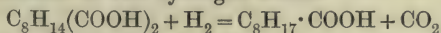
The acids boiling above 220° were submitted to systematic, repeated fractional distillation, using small columns made for us by Geissler especially for this purpose; by this means, we were able to isolate two acids which boiled remarkably constantly at 230—232° and 240—242° respectively.

The acid boiling at 230—232°, on analysis, gave numbers agreeing

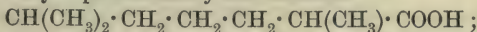
\* The numbers given in this column are the true boiling points of the acids; the fractions obtained and actually examined and analysed are given in the experimental part of this paper.

well with the formula  $C_7H_{15} \cdot COOH$ , and although it may contain small quantities of the homologues of lower and higher boiling point, we think it improbable, and are also disinclined to believe that it consists of isomeric acids of the above formula. This acid, on oxidation with permanganate, yields, besides fatty acids of low boiling point (consisting apparently of acetic and propionic acids), succinic acid and  $\alpha$ -methylglutaric acid,  $CH_3 \cdot CH(COOH) \cdot CH_2 \cdot CH_2 \cdot COOH$ , and we have suggested the formula  $(CH_3)_2CH \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot COOH$  as probably representing its constitution.

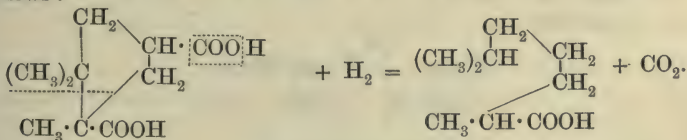
The acid boiling at  $240-242^\circ$  is a very interesting compound, since on analysis it gives numbers agreeing with the formula  $C_8H_{17} \cdot COOH$ , and this is confirmed by the analysis of the silver salt,  $C_8H_{17} \cdot COOAg$ . Such an acid would be derived from camphoric acid by the elimination of carbonic anhydride, and splitting of the ring by the addition of two hydrogen atoms.



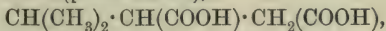
This acid, on oxidation, yields an acid which, from its properties, is evidently  $\alpha$ -methylglutaric acid, and its constitution, therefore, is in all probability represented by the formula



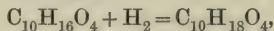
this formula could easily be derived from camphoric acid, on the assumption that it has the constitution represented here,\* as follows:



The oily acids A and B contained, besides large quantities of isopropylsuccinic acid (pimelic acid),



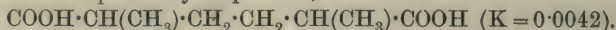
a very interesting dibasic acid of the composition  $C_{10}H_{18}O_4$ , which crystallises well, melts at  $106^\circ$ , and gives a silver salt of the composition  $C_8H_{16}(COOAg)_2$ . This acid, which must have been formed by the reduction of camphoric acid at the high temperature of the melt, with consequent splitting of the ring



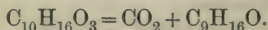
we have named *dihydrocamphoric acid*. It differs in nearly all its properties from camphoric acid, and has a much higher dissociation constant,

\* This formula for camphoric acid is used in this paper because, from results obtained by one of us in the examination of sulphocamphylic acid, and which are shortly to be communicated to the Society, it seems the most probable.

the value found by Dr. Ewan ( $K=0.00415$ ) being nearly twice as great as that of camphoric acid ( $K=0.0025$ ), and almost identical with that of  $\alpha\alpha_1$ -dimethyladipic acid,

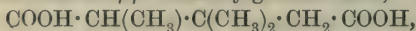


When treated with acetic anhydride, this acid is converted into a liquid which, from the analysis, appears to be the anhydride, and this, when heated, is decomposed in a remarkable manner into carbonic anhydride and a ketone of the formula  $\text{C}_9\text{H}_{16}\text{O}$



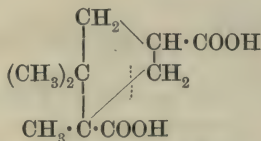
This new ketone, which we have called *dihydrocamphoketone*, is a liquid which boils at  $180-181^\circ$ , and has a most penetrating odour of peppermint; it is well characterised by forming a beautifully crystalline *semicarbazone* which melts at  $202-203^\circ$ .

It is readily oxidised by boiling with dilute nitric acid, with formation of succinic acid, oxalic acid, and an acid,  $\text{C}_8\text{H}_{14}\text{O}_4$ , which melts at  $94^\circ$ , and gives an anilic acid melting at  $159^\circ$ . These properties indicate that this acid is  $\alpha\beta\beta$ -trimethylglutaric acid,

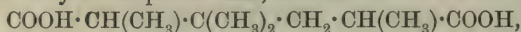


which Balbiano (*Berichte*, 1895, 28, 1507) obtained from camphoric acid, and which, he states, melts at  $94-95^\circ$  and gives an anilic acid melting at  $159^\circ$ .

Starting from the constitution of camphoric acid which was suggested on p. 5, namely,



there seems to be only one formula which satisfactorily explains the reactions of dihydrocamphoric acid, and that is



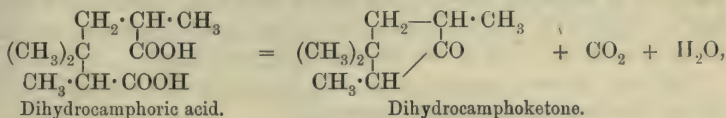
a formula obtained by adding on two atoms of hydrogen at the point marked  $\vdots$  in the formula for camphoric acid given above; this represents the substance as  $\alpha\alpha_1\beta\beta$ -tetramethyladipic acid, and experiments are now being carried out with the object of preparing this acid synthetically, and comparing its properties with those of dihydrocamphoric acid.

It has already been stated that the constant for the electrical conductivity of this acid ( $K=0.00415$ ) agrees very closely with that of  $\alpha\alpha_1$ -dimethyladipic acid ( $K=0.0042$ ), and this fact, taken in conjunction with the great readiness with which the acid loses carbonic anhydride with formation of the cyclic ketone, *dihydrocamphoketone* (compare especially J. Brecht and M. v. Rosenberg, *Annalen*, 1896, 289, 1-14,



and J. Wislicenus, *ibid.*, 1893, 275, 309), seems to us to show conclusively that the acid is a derivative of adipic acid.

The formation of dihydrocamphoketone would then be expressed thus



and this view of the constitution of dihydrocamphoketone is a very probable one, since the formula readily explains the formation of  $\alpha\beta$ -trimethylglutaric acid by the oxidation of the ketone.

Dihydrocamphoketone is very similar, in many of its properties, to camphorophorone, the ketone which is formed when the calcium salt of camphoric acid is distilled, and which boils at 200—205° and has a penetrating odour of peppermint. The latter ketone, on oxidation, yields  $\alpha$ -methylglutaric acid, formic acid, and acetic acid (Königs, Eppens, *Berichte*, 25, 266), a decomposition which has led Bredt (*loc. cit.*) to

propose the formula,  $\begin{array}{c} \text{CH}_2 \cdot \text{C}[\text{C}(\text{CH}_3)_2] \\ | \\ \text{CH}_2 - \text{CH}(\text{CH}_3) \end{array} > \text{CO}$ , for camphorophorone. If this formula should prove correct, it is probable that, in spite of the similarity in properties, there is no close connection between this substance and dihydrocamphoketone.

## II. The Substances formed when Camphoric Acid is Fused with Soda.

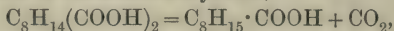
The fusion of 4 kilos. of camphoric acid with soda was carried out under the same conditions and in the same apparatus as was used in the experiments with caustic potash, and the melts were worked up in the first instance in a very similar manner to the potash melts. The amount of acids volatile with steam in this case was very much less than that obtained from the potash melts, 5 kilos. of camphoric acid fused with potash yielded 2.3 kilos. of volatile acids, whereas from 4 kilos. fused with soda only 715 grams were obtained. A great difference was also noticed in the composition of the acids from the two experiments, and this is well brought out by tables which have been introduced into the experimental part of this research (p. 33). The constitution of the various acids which were obtained by fractionating the 715 grams from the soda melts was very carefully investigated, in order to determine whether any difference could be noted in the nature of these acids as compared with those from the potash melts, but this does not appear to be the case except in the highest fraction of all.

In fractioning the acids from the potash melts, a small quantity of an oil was obtained boiling at 240—242°, which, on analysis, was

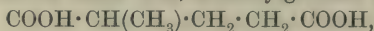


found to consist for the most part of a saturated acid of the formula  $C_8H_{17} \cdot COOH$ . From the soda melts, a comparatively much larger quantity of an acid of the same boiling point was obtained, which, however, on repeated analysis, was found not to be identical with the acid  $C_8H_{17} \cdot COOH$ , but to contain two atoms of hydrogen less, and to be an unsaturated acid of the formula  $C_8H_{15} \cdot COOH$ .

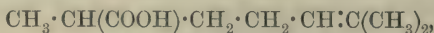
This acid, which apparently had been formed from camphoric acid by the elimination of carbonic anhydride,



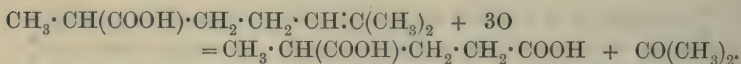
decolorises permanganate instantly in the cold, and is converted into a *dibromo-acid* of the formula  $C_8H_{15}Br_2 \cdot COOH$ , by treatment with bromine. On oxidation, first with permanganate and then with chromic acid, it yielded, besides acetic acid,  $\alpha$ -methylglutaric acid,



and we therefore suggest that its constitution may probably be expressed by the formula

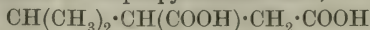


a formula which it will be seen can readily be deduced from the constitution of camphoric acid adopted in this paper, and from the suggested constitution of the acid  $C_8H_{17} \cdot COOH$  (p. 5), with which, no doubt, it is closely allied. This formula is rendered probable from the fact that a distinct odour of acetone was noticed during the oxidation with chromic acid; and the oxidation may then be assumed to have taken place in the following way :



The acetone would then, on further oxidation, yield the acetic acid which was found among the products. It should be mentioned that a careful examination of the acids boiling at  $240-242^\circ$  from the potash and soda melts has shown that the products, in both cases, contain the saturated acid  $C_8H_{17} \cdot COOH$  and the unsaturated acid  $C_8H_{15} \cdot COOH$ , traces of the former being found in the soda melts and traces of the latter in the potash melts; this difference is doubtless due to the well-known fact that potash when fused with organic substances exercises a more powerful reducing action than soda.

The examination of the acids produced on fusing camphoric acid with soda, and which were not volatile in steam, has given most interesting results. These acids, which weighed 700 grams, contained, besides considerable quantities of isopropylsuccinic acid,



(pimelic acid), and some camphoric acid, small quantities of two new acids, one crystalline and the other a syrup; these were separated

from the pimelic acid and camphoric acid only with great difficulty, and by methods which are described in detail in this paper.

The crystalline acid which melts at 119—120°, on repeated analysis, gave numbers which showed that it was a dibasic acid of the formula  $C_8H_{14}(COOH)_2$ , that it was, in fact, a new isomeride of camphoric acid.

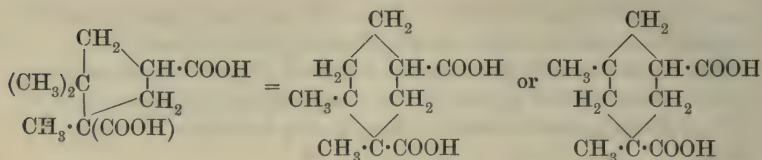
This acid which we have called *pseudo*-camphoric acid, gives well-defined salts of which the *silver* salt,  $C_8H_{14}(COOAg)_2$ , was repeatedly analysed. It yields also a crystalline *anhydride*,  $C_8H_{14} \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} O$ , which melts at 52—53°, and an anilic acid,  $COOH \cdot C_8H_{14} \cdot CO \cdot NH \cdot C_6H_5$ , melting at 208°. Pseudocamphoric acid does not decolorise alkaline permanganate except on long standing, and it is therefore, like camphoric acid, saturated, but it differs from the latter in that when treated with sulphuric acid, it does not evolve carbon monoxide and yield a sulphonic acid of the nature of sulphocamphylic acid.

Before Aschan's classical researches on the camphoric acids had been published (*Berichte*, 27, 2001, *Chemisches Centralblatt*, 1895, 51, 967), thirteen isomeric forms of these acids had been described: Aschan, however, showed that in reality there were only six modifications namely, the four active acids *d*- and *l*-camphoric acid and *d*- and *l*-isocamphoric acid, and the two inactive racemoid forms, *i*-camphoric acid and *i*-isocamphoric acid. The active camphoric acids melt at 187° and *i*-camphoric acid at 202—203°, the active isocamphoric acids have lower melting points, namely, 171—172° and *i*-isocamphoric acid melts at 191°. The camphoric acids belong to the *cis*-form and yield anhydrides, whereas the isocamphoric acids which are *trans*-modifications do not do so.

These are the only modifications possible on the assumption that camphoric acid has the formula suggested by Bredt or the formula adopted in this paper.

It will be seen that our *pseudocamphoric acid* is quite different in its properties from any of the above acids; moreover, that it is not a mixture of a camphoric acid and an isocamphoric acid, such as has been, in previous cases, found to melt at about 130°, and therefore described as new, is shown by the fact that our acid, when treated with acetyl chloride according to Aschan's directions, remains unaltered, whereas such a mixture would yield the anhydride of the camphoric acid, whilst the isocamphoric acid remained unchanged.

It seems very probable that, in the formation of pseudocamphoric acid from camphoric acid, the 5 ring in the latter acid has been converted into a 6 ring by the introduction of one of the methyl groups of the complex  $(CH_3)_2C=$  thus.



These formulæ represent pseudocamphoric acid as a derivative of hexahydrophthalic acid on the one hand, and on the other as a substituted glutaric acid, and either view agrees well with the properties of the acid, and especially with the fact that it yields a well characterised anhydride and anilic acid.

The syrupy acid mentioned on p. 8 as having been obtained from that portion of the acids not volatile with steam, is a substance having very interesting properties. It is a very viscid, colourless syrup which distils remarkably constantly at 254—257° (50 mm.), and, on examination, has been found to consist of an acid of the formula  $\text{C}_9\text{H}_{16}\text{O}_4$  very soluble in water, mixed with very small quantities of an oil insoluble in water, properties which make it easy to separate the two.

The acid  $\text{C}_9\text{H}_{16}\text{O}_4$  differs from all the other substances described in this paper in that, in spite of its high molecular weight, it is unusually soluble, in fact almost miscible with water. It is a dibasic acid which yields a *silver* salt,  $\text{C}_7\text{H}_{14}(\text{COOAg})_2$ , and although it distils almost without change, that is, without forming an anhydride, it does yield an anhydride,  $\text{C}_7\text{H}_{14} \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{O}$ , boiling at 185—190° (35 mm.) when digested with acetic anhydride. We have not, so far, been able to obtain any clue to the nature of this acid.

This research was commenced in 1893 in the laboratories of Owens College, and since 1895 it has been carried on uninterruptedly both in Owens College and in the chemical laboratory of St. Thomas's Hospital, and we wish to express our hearty thanks to Messrs. W. H. Bentley, G. Haworth, J. L. Heinke, F. H. Lees, and others for valuable help in carrying out this difficult investigation.

## EXPERIMENTAL.

### FUSION OF CAMPHORIC ACID WITH CAUSTIC POTASH.

*Description of the Melting.*—Five kilos. of camphoric acid were treated in the following manner. Five hundred grams of camphoric acid were mixed with 4 kilos. of caustic potash containing 85 per cent. KOH in a large iron pot, and the whole well moistened with water; the pot was then rapidly heated with two very large Fletcher burners, the contents



being meanwhile well stirred. As the temperature gradually rose, the mass assumed a pasty consistency, and at about  $170^{\circ}$  to  $180^{\circ}$  bubbles appeared round the edge of the melt, increasing in number with the rise in temperature; water was given off and a small amount of a light coloured scum formed on the surface. At  $250^{\circ}$ , the melt set to a hard mass and could only be stirred with difficulty; great care was required at this stage to prevent charring. On continuing to heat, the melt again became quite liquid at about  $300^{\circ}$ , and just above  $360^{\circ}$  began to give off large quantities of hydrogen, at the same time a penetrating aromatic odour somewhat resembling that of menthol was observed. The evolution of hydrogen continued for from 2— $2\frac{1}{2}$  hours, and the whole operation lasted from 3— $3\frac{1}{2}$  hours. As soon as hydrogen ceased to be evolved, the melt was poured on to shallow iron trays and allowed to cool, when it soon solidified to a hard, brittle cake of a greenish colour.

*Working up of the Product.*—When cold, the melt was broken up and placed in a lead-lined iron vessel (specially fitted up for steam distillation), a large amount of water added, and steam passed through until the whole was dissolved. The lid of the vessel was then fastened down, and through a tap in the lid a quantity of 33 per cent. sulphuric acid was run in somewhat more than sufficient (this was calculated from experiments made with small samples of the different melts) to combine with the caustic potash used, and the whole submitted to steam distillation until the condensed water had only a very slight acid reaction. The acid distillate was neutralised with caustic soda and evaporated to dryness.

By this means, 4 kilos. of sodium salts were obtained, which were dissolved in the least possible quantity of water, strongly acidified with hydrochloric acid and extracted with ether; the ethereal solution was dried over calcium chloride and the ether evaporated; the residue weighed 2.3 kilos. and was treated in the manner described in detail on page 12.

*Residue from the Steam Distillation.*—The residue from the distillation with steam, on cooling, deposited large quantities of potassium sulphate; this was filtered off, and the filtrate neutralised with caustic soda and evaporated to about one-third its bulk in large, flat copper pans, heated by steam. The salts which separated from this concentrated liquor contained much organic matter, and on treatment with hydrochloric acid and ether in the manner just described, yielded 510 grams of a pale yellow oil (A).

Lastly, the filtrate from the above salt was evaporated to dryness; at a later date, this solid residue was dissolved in water, strongly acidified with hydrochloric acid, and treated with ether as above, when 346 grams of a dark yellow oil (B) was obtained.



The process adopted in working up the oils (A) and (B) is described on pages 22 and 23.

*Volatile Acids formed by the Fusion of Camphoric Acid with Potash.*

The 2·3 kilos. of crude acids which had been volatilised with steam (p. 11) were now carefully fractionated, using a column, with the following results.

Fraction.	Weight in grams.
50—100°	296
100—125	663
125—135	515
135—150	387
above 150	325

The fraction 50—100° contained water and ether; the ethereal solution separated from the water was carefully dried over anhydrous sodium sulphate; the fractions 100—125°, 125—135°, and 135—150° were also carefully dried over sodium sulphate, and the whole was then repeatedly distilled, the acids, after each distillation, being again dried over anhydrous sodium sulphate. The appended table gives the result of this treatment.

Fraction.	Weight in grams after 2nd distillation.	Weight in grams after 3rd distillation.	Weight in grams after 4th distillation.
50—100°	13	—	—
100—125	501	689	701
125—135	Not distilled	310	330
135—150	„	360	285
above 150			20

The acids boiling above 150° gave the following results on fractionation.

Fraction.	Weight in grams after 1st distillation.	Weight in grams after 2nd distillation.
below 150°	2	15
150—160	12	58
160—170	68	40
170—180	59	33
180—190	41	36
190—200	42	31
200—210	42	42
210—220	43	48
220—230	33	30
230—240	22	14
above 240	22	32

From the acids boiling above  $240^{\circ}$ , a small amount of solid matter crystallised out on standing, which, when separated from the liquid and dried, was found to have a melting point of  $114^{\circ}$ , corresponding with that of pimelic acid (isopropylsuccinic acid). The presence of this acid could only be accounted for by assuming that it was to some extent volatile with steam, and, in order to test this supposition, the following experiment was made.

Five grams of pimelic anhydride were dissolved in caustic soda, acidified with sulphuric acid, and steam distilled for  $1\frac{3}{4}$  hours. The distillate, after being neutralised with caustic soda, evaporated, acidified with sulphuric acid, extracted with ether, &c., gave 0.2 gram of a crystalline solid having a melting point of  $114^{\circ}$ , which is that of pimelic acid. This shows that pimelic acid is to some extent carried over during steam distillation.

It was thought that a separation of pimelic acid from the fatty acids might be effected, if the ammonium salts were distilled with steam. The salts of the fatty acids would by this means be dissociated into ammonia and the free acids which would distil over, whereas the ammonium salt of pimelic acid might be expected to remain undecomposed.

On making a blank experiment in this way with 20 grams of pimelic anhydride, it was found that the ammonium salt of pimelic acid is not decomposed during steam distillation.

In order to test this method of separation further, a considerable amount of acids from which a small quantity of the crystalline substance, melting at  $114^{\circ}$ , had been obtained, was dissolved in ammonia and steam distilled until no more acid came over with the condensed water. The ethereal extract from the acidified residue left in the retort solidified completely on standing, and the crystals melted at  $114^{\circ}$  (pimelic acid). These experiments showed that the acids boiling above  $150^{\circ}$  must contain pimelic acid, and as it was necessary to get rid of this substance, the whole of the fatty acids boiling above this temperature was dissolved in ammonia and steam distilled. The total amount of crude pimelic acid obtained from the residue was about 45 grams. During the distillation, the first portion which passed over was strongly alkaline (from the presence of ammonia) and from this liquid a small amount of an oil separated (about 2 grams); this was extracted with ether, but the quantity was too small to allow of its nature being investigated. The combined distillates from the steam distillation were neutralised with caustic soda, evaporated, acidified and treated with ether, &c., as described on p. 11, and fractionated.

Fraction.	Weight in grams before the ammonium salt purification.	Weight in grams after the ammonium salt purification.	Weight in grams of acid from residue after distillation.
150—160°	58	31	20
160—170	40	25	
170—180	33	25	
180—190	36	35	
190—200	31	20	
200—210	42	43	25
210—220	48	32	
220—230	30	54	
230—240	14	20	
above 240	32	6	

*The Fraction 100—125° contains Acetic Acid,  $\text{CH}_3 \cdot \text{COOH}$ .*—In order to thoroughly dry this fraction, it was mixed with an equal volume of concentrated sulphuric acid, allowed to stand for 24 hours, and then distilled; this operation was repeated four times, and finally, after several fractional distillations, a considerable quantity of pure acetic acid was isolated which solidified on cooling with ice. The silver salt prepared from this, after recrystallisation from water, gave the following result on analysis.

0.1996, on ignition, gave 0.1290 Ag. Ag = 64.62.

$\text{CH}_3\text{COOAg}$  requires Ag = 64.67 per cent.

The acid was further characterised by converting it into ethylic acetate and acetanilide.

*The Fraction 135—150° contains Propionic Acid,  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$ .*—After drying with sulphuric acid and repeated very careful fractional distillation, a portion was isolated which boiled constantly at 140°, and, on analysis, was shown to be propionic acid.

0.1628 gave 0.2909  $\text{CO}_2$  and 0.1224  $\text{H}_2\text{O}$ . C = 48.72; H = 8.35.

$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$  requires C = 48.64; H = 8.10 per cent.

The silver salt was also analysed.

I. 0.1540, on ignition, gave 0.0918 Ag. Ag = 59.61.

II. 0.2689 „ „ „ 0.1602 Ag. Ag = 59.57.

0.2689 gave 0.1942  $\text{CO}_2$  and 0.0658  $\text{H}_2\text{O}$ . C = 19.70; H = 2.71.

$\text{C}_3\text{H}_5\text{O}_2\text{Ag}$  requires Ag = 59.66; C = 19.89; H = 2.76 per cent.

*The Fraction 150—160° contains Isobutyric Acid.*—Hlasiwetz and Grabowski considered that the acid formed by the action of fused potash on camphoric acid consisted of butyric acid. We have, however, failed to substantiate this statement, as we have not succeeded in isolating any butyric acid, although, on the other hand, we find that *iso*-butyric acid is formed in considerable quantities during the fusion.



As the boiling points of the two butyric acids are near to one another (normal acid,  $163^{\circ}$ ; *iso*-acid,  $150^{\circ}$ ) it was feared that, if both were present, distillation alone would not separate them. Wechsler's\* method (*Monatshefte*, July, 1893, 462) was therefore resorted to.

For this purpose, the whole of the fraction  $150\text{--}160^{\circ}$  was neutralised with standard caustic soda, one-third of the amount of standard sulphuric acid necessary to neutralise the soda was added, and the mixture steam distilled until the distillate was no longer acid. According to Wechsler, under these conditions, the acid of higher boiling point comes over first; so that the distillate should contain butyric acid, if any were present. An analysis of the fraction  $160\text{--}166^{\circ}$  of the acids obtained from the distillate gave the following numbers.

0.1918 gave 0.3980  $\text{CO}_2$  and 0.1631  $\text{H}_2\text{O}$ .  $\text{C} = 56.62$ ;  $\text{H} = 9.43$ .

$\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{C} = 54.54$ ;  $\text{H} = 9.09$ .  $\text{C}_5\text{H}_{10}\text{O}_2$  requires  $\text{C} = 58.82$ ;  $\text{H} = 9.80\%$ .

Evidently the substance is a mixture of probably isobutyric acid (or butyric acid) and isovaleric acid.

To the residue of the distillation, another portion of the standard acid, equal to one-third of the soda solution originally used, was added, and the whole again distilled in steam. The distillate was heated with excess of calcium carbonate, filtered, and the clear filtrate concentrated on the water bath, when, on cooling, well-defined, white, feathery crystals separated. A portion of the clear mother liquor, which had a syrupy consistency, was heated at  $100^{\circ}$  in a closed tube, but only a minute quantity of solid matter was precipitated, showing that not more than a trace of the calcium salt of normal butyric acid could have been present.

The acid, recovered from the calcium salt in the usual way, by acidifying and extracting with ether, was submitted to fractional distillation, and the portion boiling between  $152^{\circ}$  and  $153^{\circ}$  was analysed.

0.1561 gave 0.3089  $\text{CO}_2$  and 0.1250  $\text{H}_2\text{O}$ .  $\text{C} = 53.98$ ;  $\text{H} = 8.9$ .

$\text{C}_4\text{H}_8\text{O}_2$  requires  $\text{C} = 54.54$ ;  $\text{H} = 9.09$  per cent.

The calcium salt prepared from this acid was also analysed.

0.1264, dried at  $100^{\circ}$ , gave 0.0828  $\text{CaSO}_4$ .  $\text{Ca} = 18.98$ .

0.1708 of the air-dried salt lost 0.0440  $\text{H}_2\text{O}$  at  $155^{\circ}$ .  $\text{H}_2\text{O} = 25.76$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}$  requires  $\text{Ca} = 18.69$  per cent.

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 25.17$ .  $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 29.60$  per cent.

This determination of the water of crystallisation agrees well with that of the calcium salt obtained from the soda melts; but according

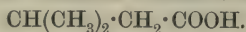
\* This method, although in some cases valuable, is not so trustworthy as might be supposed from the description given by Wechsler, as detailed experiments, carried out by one of us, show (*Trans.*, 1897, 71, 580).



to Chancel and Parmentier (*Compt. rend.*, 1887, 104, 477) calcium isobutyrate contains  $5\text{H}_2\text{O}$ . An examination of the calcium salt prepared from pure isobutyric acid showed that, if left exposed to the air, it loses some of its water of crystallisation; this accounts for the numbers obtained in the above analysis being low.

These experiments prove conclusively that isobutyric acid is one of the acids formed during the fusion of camphoric acid with caustic potash.

*The Fraction 170—180° contains Isovaleric Acid,*



—The very disagreeable smelling oily acids boiling within these limits were repeatedly fractionated, when a considerable quantity was obtained boiling at  $175\text{—}180^\circ$ ; the product, on analysis, gave the following result.

0.1207 gave 0.2592  $\text{CO}_2$  and 0.1092  $\text{H}_2\text{O}$ .  $\text{C} = 58.57$ ;  $\text{H} = 10.04$ .

$\text{C}_5\text{H}_{10}\text{O}_2$  requires  $\text{C} = 58.82$ ;  $\text{H} = 9.80$  per cent.

The whole of this fraction was converted into the anilide which was purified by crystallisation from light petroleum (b. p.  $100\text{—}120^\circ$ ). It formed shining, white needles which melted at  $109.5\text{—}110.5^\circ$ .

I. 0.1141 gave 8.1 c.c. moist nitrogen at  $12^\circ$  and 752 mm.  $\text{N} = 8.33$ .

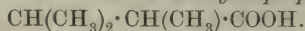
II. 0.1154 „ 7.9 „ „  $13.5^\circ$  „ 769 mm.  $\text{N} = 8.16$ .

$\text{C}_{11}\text{H}_{15}\text{NO}$  requires  $\text{N} = 7.91$  per cent.

According to Chiozza (*Ann.*, 1852, 84, 109), the melting point of iso-valerianilide is  $115^\circ$ ; whilst Schmidt and Sachtleben (*Ann.*, 1878, 193, 102) state that the anilide prepared from synthetical isobutylformic (isopropylacetic) acid melts at  $100^\circ$ .

In order to test these statements, isopropylacetic acid was prepared from ethylic isopropylmalonate. This ethereal salt after careful fractionation was hydrolysed with alcoholic potash, the dibasic acid distilled to eliminate carbon dioxide, and the distillate fractionated. A portion of the pure acid boiling at  $175^\circ$  was converted into the anilide, which, after repeated recrystallisation from light petroleum, melted at  $109\text{—}111^\circ$ ; this agrees with the melting point of the acid prepared from the fusion of camphoric acid with caustic potash, proving that the acid described above is isovaleric acid.

*The Fraction 180—200° contains Methylisopropylacetic Acid,*



—The fraction of the fatty acids boiling between  $180^\circ$  and  $200^\circ$  (about 70 grams) was 12 times very carefully fractionated, the following fractions being ultimately obtained.

$180\text{—}183^\circ = 5$  grams       $189\text{—}192^\circ = 15$  grams

$183\text{—}186^\circ = 8$  „       $192\text{—}195^\circ = 11$  „

$186\text{—}189^\circ = 14$  „       $195\text{—}198^\circ = 7$  „

The fraction 186—192°, which weighed 29 grams, was converted into the anilide in the usual way, and this, on standing for some days in an ice chest over sulphuric acid in a vacuum desiccator, deposited crystals which, after being left in contact with porous porcelain for a fortnight, were purified by repeated crystallisation from dilute methylic alcohol. The anilide thus obtained melted sharply at 75°, and gave the following numbers on analysis.

0·1608 gave 10·4 c.c. moist nitrogen at 15° and 750 mm.  $N = 7·47$ .

$C_5H_{11} \cdot CO \cdot NH \cdot C_6H_5$  requires  $N = 7·33$  per cent.

This pure anilide was digested with concentrated hydrochloric acid, and the regenerated acid, after extraction with ether and drying over calcium chloride, was distilled, when the whole passed over at 189—191° (766 mm.) and gave, on analysis, the following numbers.

0·1451 gave 0·3288  $CO_2$  and 0·1338  $H_2O$ .  $C = 61·82$ ;  $H = 10·24$ .

$C_5H_{11} \cdot COOH$  requires  $C = 62·07$ ;  $H = 10·34$  per cent.

The silver salt prepared from the ammonium salt by precipitation, is amorphous and insoluble.

0·1340 gave, on ignition, 0·0645 Ag.  $Ag = 48·13$

$C_5H_{11} \cdot COOAg$  requires  $Ag = 48·43$  per cent.

In order to further characterise this acid, it was converted into the paratoluidide,  $C_5H_{11} \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$ , by treating the acid chloride with paratoluidine. As the crude product of the action did not crystallise readily, it was ground up for some days successively with small quantities of dilute sodium carbonate solution, and dilute hydrochloric acid; it ultimately became quite hard, and was then purified by recrystallisation from light petroleum (b. p. 60—80°) from which it separated in colourless needles melting at 103—104°.

0·1522 gave 8·8 c.c. moist nitrogen at 14° and 752 mm.  $N = 6·73$ .

$C_5H_{11} \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3$  requires  $N = 6·83$  per cent.

As the boiling point of this acid coincides exactly with that of methylisopropylacetic acid ( $\alpha\beta\beta$ -trimethylpropionic acid) which one of us had previously prepared (Trans., 1896, 69, 1476), it seemed probable that the two acids might be identical. In order to test this, synthetic methylisopropylacetic acid boiling at 189—190° was converted into the anilide and paratoluidide, which were found to be identical in every respect with those prepared from the acid described above. The acid obtained by the fusion of camphoric acid with potash, and boiling at 189—191°, is therefore methylisopropylacetic acid.

*Examination of the Acids Boiling at 200—220°.*

It will be seen from the table on page 14 that no less than 75 grams of acid of the fraction distilling between 200 and 220° had been obtained; and it seemed probable that a careful examination of it might furnish very interesting results. Accordingly, the mixture was very carefully fractionated (12 times) with the following results.

200—203° = 6 grams	209—212° = 19 grams
203—206 = 10 „	212—215 = 9 „
206—209 = 21 „	215—218 = 4 „

The fraction 206—212°, converted into the acid chloride in the usual way, distilled entirely between 115° and 120° (200 mm.). The oily anilide prepared from this, after being kept for some days at 0°, deposited a semi-solid mass of crystals. This, when placed on porous porcelain, left an almost colourless crystalline cake, which was purified by recrystallisation from light petroleum (b. p. 60—90°); in this way, a very sparingly soluble anilide was easily isolated in a beautifully crystalline condition, and melting sharply at 105—105·5°.

0·2146 gave 13·2 c.c. moist nitrogen at 20° and 754 mm.  $N = 6·98$ .

$C_6H_{13} \cdot CO \cdot NH \cdot C_6H_5$  requires  $N = 6·83$  per cent.

The anilide was now decomposed by digestion with strong hydrochloric acid in a reflux apparatus for about two days; the oily acid, extracted with pure ether in the usual way, was purified by fractionation, when almost the whole distilled at 209—210° as a colourless oil.

0·1494 gave 0·3521  $CO_2$  and 0·1425  $H_2O$ .  $C = 64·27$ ;  $H = 10·60$ .

0·1384 „ 0·3269  $CO_2$  „ 0·1338  $H_2O$ .  $C = 64·42$ ;  $H = 10·74$ .

0·1522 „ 0·3604  $CO_2$  „ 0·1493  $H_2O$ .  $C = 64·58$ ;  $H = 10·91$ .

$C_6H_{13} \cdot COOH$  requires  $C = 64·61$ ;  $H = 10·77$  per cent.

The silver salt of this acid is a white, caseous, insoluble precipitate, which, after washing well with water, alcohol, and ether, gave the following results on analysis.

0·1081 gave, on ignition, 0·0492 Ag.  $Ag = 45·51$ .

0·1622 „ „ 0·0738 Ag.  $Ag = 45·49$ .

$C_6H_{13} \cdot COOAg$  requires  $Ag = 45·57$ .

These results prove conclusively that the acid boiling at 209—210° is a heptylic acid,  $C_6H_{13} \cdot COOH$ .

As far as we have been able to find out, there have been comparatively few acids of this composition prepared, the following being a table of the known isomerides.

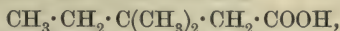


- (1) Normal heptylic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{COOH}$  ..... b. p.  $220 \cdot 4^\circ$   
 (2) Methylbutylacetic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{COOH}$  ,, 210  
 (3) *iso*-Oenanthic acid, constitution unknown ..... b. p. 210—213  
 (4) *iso*-Amylacetic acid,  $\text{CH}(\text{CH}_3)_2 \cdot [\text{CH}_2]_3 \cdot \text{COOH}$  ,, 208—210  
 (5) Methyl-diethylacetic acid,  $\text{C}(\text{C}_2\text{H}_5)_2 \cdot [\text{CH}_3] \cdot \text{COOH}$  ,, 207—208  
 (6) Ethylpropylacetic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{COOH}$  b. p.  $209 \cdot 2$   
 (7) Methylisobutylacetic acid,  $\text{CH}_3 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{COOH}$  ... ,, 205  
 (8) Methylisopropylpropionic acid,  
 $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{COOH}$  (?) ..... ,, 220

It will be seen from this table that several of these acids boil at the same temperature as our hexylic acid, but as the anilides of the acids boiling between  $207$ — $213^\circ$  have not been prepared, it is impossible to decide whether or not any one of these is identical with the acid from camphoric acid.

At first we thought it probable that our acid might be isoamylacetic acid, and we therefore prepared this acid, and converted it into its anilide; this, however, melts at  $75^\circ$ , and is quite different in its solubilities and appearance from our anilide.

We are for several reasons inclined to think that our acid is a dimethylethylpropionic acid of the formula



and we propose to synthesise this acid with the view to decide this point.

#### *Examination of the Acids Boiling above $220^\circ$ .*

The portion of the acids boiling above  $220^\circ$ , weighing about 80 grams, was submitted to repeated fractionation, and ultimately the following quantities were obtained.

220—225° = 7 grams.	235—240° = 9 grams.
225—230 = 14 ,,	240—245 = 15 ,,
230—235 = 15 ,,	245—250 = 6 ,,

As during the distillations it was noticed that the temperature always remained constant for a considerable time at  $230$ — $232^\circ$  (750 mm.), a small quantity boiling at this temperature was converted into the anilide, in the hope that it might crystallise well, but this was not the case, and the same remark applies to the fraction  $240$ — $245^\circ$ . The fraction  $225$ — $235^\circ$  was now submitted 10 times to most careful fractionation, and ultimately 9 grams of an acid were obtained, boiling almost constantly at  $230$ — $232^\circ$  (750 mm.). On analysis, it gave the following results.

0.1074 gave 0.2602  $\text{CO}_2$  and 0.1032  $\text{H}_2\text{O}$ . C = 66.09; H = 10.68.

0.1610 ,, 0.3923  $\text{CO}_2$  ,, 0.1591  $\text{H}_2\text{O}$ . C = 66.44; H = 10.99.

$\text{C}_7\text{H}_{15} \cdot \text{COOH}$  requires C = 66.66; H = 11.11 per cent.



The slightly alkaline solution of the ammonium salt was precipitated fractionally with silver nitrate, and the three fractions of silver salt thus obtained gave the following results on analysis.

I.	0.1676	gave, on ignition,	0.0720 Ag.	Ag = 42.95.
II.	0.1483	„ „	0.0641 Ag.	Ag = 43.23.
III.	0.2224	„ „	0.0965 Ag.	Ag = 43.39.
$C_7H_{15} \cdot COOAg$ requires Ag = 43.03 per cent.				

This close agreement of the three fractions of the silver salt with the formula  $C_7H_{15} \cdot COOAg$  appears to indicate that the fraction 230—232° consists either of a pure acid or a mixture of isomeric acids of this formula. The former alternative seems to us to be the more probable.

*Oxidation of the Acid Boiling at 230—232°.*—In order, if possible, to obtain some clue as to the nature of this acid, the whole quantity which remained after the above analyses had been made was submitted to oxidation with potassium permanganate. As the acid is only very slowly attacked by alkaline permanganate in the cold, the solution of the acid in sodium carbonate was heated to boiling, and then small quantities of the oxidising agent added, until the oxidation appeared to become sluggish. The excess of permanganate was then destroyed by sodium hydrogen sulphite, the manganese precipitate removed by filtration, and the filtrate and washings concentrated; the liquid was then acidified with sulphuric acid and distilled with steam as long as any unchanged acid passed over. The distillate was made alkaline and oxidised as before, the operation being repeated until no unchanged acid distilled with the steam. The last steam distillate, on being neutralised with carbonate of soda and evaporated to dryness, gave a considerable quantity of a sodium salt the acid from which nearly all passed over below 150° and appeared to consist mainly of acetic and propionic acids.

The residual liquors resulting from the oxidations were concentrated, acidified with dilute sulphuric acid, saturated with ammonium sulphate, and extracted 10 times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited an almost colourless oil which, on distillation under reduced pressure (40 mm.), yielded a considerable quantity of a fraction boiling at about 160—175°; as this dissolved with difficulty in sodium carbonate solution, it evidently consisted mainly of an anhydride. The whole was, therefore, dissolved in hot dilute caustic soda, a small quantity of a neutral oil removed by ether, and the acid again extracted from the solution after acidification, in the usual way. The oily acid thus obtained, when kept for some weeks in an ice chest, deposited crystals which were dried on porous porcelain, dissolved in a little water and the solution saturated with hydrogen chloride. In a short time, colourless crystals

separated which, after recrystallisation, melted at  $180^{\circ}$  and were found on analysis to consist of succinic acid.

0.1450 gave 0.2160  $\text{CO}_2$  and 0.0688  $\text{H}_2\text{O}$ .  $\text{C} = 40.63$ ;  $\text{H} = 5.27$ .

$\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  requires  $\text{C} = 40.68$ ;  $\text{H} = 5.08$  per cent.

The mother liquor from the succinic acid, when allowed to evaporate nearly to dryness over potash in a vacuum desiccator, deposited nodular crystals and some leaflets of succinic acid; the former were easily separated mechanically and after twice crystallising from hydrochloric acid were analysed.

0.1002 gave 0.1803  $\text{CO}_2$  and 0.0628  $\text{H}_2\text{O}$ .  $\text{C} = 49.10$ ;  $\text{H} = 6.97$ .

$\text{C}_6\text{H}_{10}\text{O}_4 = \text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  requires  $\text{C} = 49.32$ ;  $\text{H} = 6.85$  per cent.

The melting point of the crystals was  $75-77^{\circ}$ , and the general appearance and properties of the acid indicated that it was  $\alpha$ -methylglutaric acid (m. p.  $77-78^{\circ}$ ).

In order to confirm this, the remainder of the acid was converted into the anilic acid, which melted at  $112-113^{\circ}$ ; Auwers (*Annalen*, 292, 210) gives  $114-115^{\circ}$  as the melting point of methylglutaranilic acid. It seems, therefore, that the principal products of the oxidation of the acid boiling at  $230-232^{\circ}$  are succinic acid,  $\alpha$ -methylglutaric acid, and fatty acids of low boiling point. This acid does not appear to be identical with any of the known acids,  $\text{C}_8\text{H}_{16}\text{O}_2$ , and we are inclined to believe that its constitution is represented by the formula  $^*\text{CH}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , or methylisopropylbutyric acid, in which case, if oxidation took place at the carbon atom marked \*, the formation of methylglutaric acid under these conditions could be readily understood.

It will be seen from the table given at the head of this section that a considerable quantity (15 grams) of the acids boiled at about  $240-245^{\circ}$ , and in order to examine this portion the fraction  $235-250^{\circ}$ , weighing 30 grams, was very carefully fractionated (5 times); in this way, about 9 grams of an acid were obtained boiling at  $240-242^{\circ}$ , and giving the following results on analysis.

0.1228 gave 0.3090  $\text{CO}_2$  and 0.1234  $\text{H}_2\text{O}$ .  $\text{C} = 68.69$ ;  $\text{H} = 11.16$ .

$\text{C}_8\text{H}_{17} \cdot \text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

On examining this acid, it was found that it contained a small quantity of an unsaturated compound, undoubtedly the acid  $\text{C}_8\text{H}_{15} \cdot \text{COOH}$  referred to in describing the acids obtained from camphoric acid by fusion with caustic soda (p. 36). In order to remove this, the whole of the fraction  $240-242^{\circ}$  was dissolved in dilute sodium carbonate,

mixed with ice, and, while well agitated with a turbine (and also by passing a rapid current of carbonic anhydride), a cold saturated solution of permanganate was run in drop by drop until the colour remained permanent. The solution was then heated to boiling, filtered, the filtrate and washings of the manganese precipitate concentrated, the residue acidified, and the oily acid extracted with ether. The ethereal solution, after drying and evaporating, deposited 7.5 grams of an oil which, on distillation, passed over completely between  $240^{\circ}$  and  $245^{\circ}$ , and nearly all at  $240-242^{\circ}$ . A portion of the substance boiling at  $241^{\circ}$  was analysed.

0.1353 gave 0.3377  $\text{CO}_2$  and 0.1390  $\text{H}_2\text{O}$ .  $\text{C} = 68.07$ ;  $\text{H} = 11.41$ .

$\text{C}_8\text{H}_{17}\cdot\text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

The silver salt, prepared from the ammonium salt in the usual way, is a white, amorphous precipitate which was analysed after washing successively with water, methylic alcohol, and ether.

0.1350, on ignition, gave 0.0553 Ag.  $\text{Ag} = 40.96$ .

$\text{C}_8\text{H}_{17}\cdot\text{COOAg}$  requires  $\text{Ag} = 40.75$  per cent.

These results clearly indicate that the acid boiling at  $240-242^{\circ}$  is a fatty acid of the composition  $\text{C}_8\text{H}_{17}\cdot\text{COOH}$ , and as this acid contains only one carbon atom less than camphoric acid itself, it would be most interesting if its constitution could be elucidated. The only acids of this formula which appear to have been prepared are.

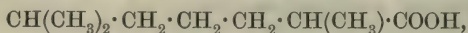
Nonylic acid (pelargonic acid),  $\text{CH}_3[\text{CH}_2]_7\cdot\text{COOH}\dots$  b. p.  $253-254^{\circ}$ .

*iso*-Nonylic acid,  $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}\dots\dots$  b. p.  $246^{\circ}$ .

Heptylacetic acid,  $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{COOH}$  b. p.  $232^{\circ}$ .

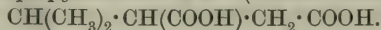
but these are obviously not identical with our acid.

With the small amount of material at our disposal, we experimented on the action of oxidising agents on the acid, and obtained, with chromic acid, an acid which showed all the properties of  $\alpha$ -methylglutaric acid, but which we did not obtain in quantity sufficient for analysis. Unfortunately, in spite of numerous experiments, no further clue to the constitution of this acid could be obtained, and we can only suggest that its constitution may possibly be expressed by the formula



or by some formula closely allied to this.

*Isopropylsuccinic Acid (Pimelic Acid),*



It was explained on p. 11 that 856 grams of oil (A and B) was extracted from the residues obtained after the volatile acids formed



during the fusion of camphoric acid with caustic potash had been distilled off with steam. The whole of this, in quantities of 50 grams at a time, was heated with acetyl chloride (100 grams) for 2 hours in a reflux apparatus, the acetyl chloride distilled off, and the residue fractionated under a pressure of 46 mm.; it began to boil at  $150^{\circ}$ , but very little passed over below  $160^{\circ}$ , then the thermometer remained constant for a long time, about 60 per cent. of the whole passing over between  $160^{\circ}$  and  $170^{\circ}$ ; the temperature then rose rapidly, the remaining liquid distilling between  $185^{\circ}$  and  $230^{\circ}$ . The fraction  $160-170^{\circ}$ , on redistillation, yielded a very large quantity of a colourless oil boiling constantly at  $164^{\circ}$  (45 mm.); this, on analysis and subsequent examination, was found to consist of pure isopropylsuccinic anhydride.

0.0974 gave 0.2105  $\text{CO}_2$  and 0.0618  $\text{H}_2\text{O}$ .  $\text{C} = 58.95$ ;  $\text{H} = 7.04$ .

$\text{C}_7\text{H}_{10}\text{O}_3$  requires  $\text{C} = 59.15$ ;  $\text{H} = 7.04$  per cent.

A portion of this anhydride was converted into the acid by dissolving it in caustic soda, acidifying, and extracting with ether, &c., when it solidified completely on cooling, and after crystallisation from benzene, melted at about  $115-116^{\circ}$ .

0.1192 gave 0.2288  $\text{CO}_2$  and 0.0804  $\text{H}_2\text{O}$ .  $\text{C} = 52.34$ ;  $\text{H} = 7.49$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

Tiemann (*Ber.*, 1895, 28, 2152) states that pimelic acid (isopropylsuccinic acid) may be obtained, melting sharply at  $118^{\circ}$ , by precipitating its chloroform solution with light petroleum, but we were not able to confirm this; the melting point was never sharp, and this is accounted for by the fact that, at its melting point, pimelic acid is slowly converted into its oily anhydride. With the large quantities of pimelic acid at our disposal, we have, when using benzene as a solvent, repeatedly obtained crystals nearly an inch in length.

#### *Dihydrocamphoric Acid, $\text{C}_{10}\text{H}_{18}\text{O}_4$*

As mentioned in the preceding section, an oil was obtained boiling at  $185-230^{\circ}$  (45 mm.); this fraction weighed about 70 grams, and its investigation has given very interesting results. The whole was boiled in a reflux apparatus with excess of caustic soda solution, when it was noticed that a small quantity of an oil, smelling strongly of peppermint, did not dissolve; this neutral oil, which may be provisionally called A, was removed by means of ether, and will be described later on in detail; in its crude state, it weighed 8 grams. The alkaline solution, when acidified with sulphuric acid, extracted with ether, &c., yielded 74 grams of a viscid oil. This was dissolved in a slight excess of ammonia, and the solution boiled with excess of a strong solution



of calcium chloride, when a large quantity of the sparingly soluble calcium pimelate was precipitated; the acid obtained from this, after purification, melted at about  $115\text{--}116^\circ$ , and consisted of pimelic acid as the results of the analysis show.

0.1240 gave 0.2380  $\text{CO}_2$  and 0.0849  $\text{H}_2\text{O}$ .  $\text{C} = 52.26$ ;  $\text{H} = 7.61$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

The solution of the ammonium salt thus completely freed from pimelic acid was acidified with sulphuric acid, extracted with ether, &c., when 47 grams of a nearly colourless oil was obtained, from which, however, only very small quantities of solid matter separated on standing. The whole was accordingly again dissolved in a slight excess of ammonia and the solution mixed with excess of zinc chloride, when an immediate and copious precipitate was formed; this was collected, and the filtrate heated to boiling, when a further quantity of a zinc salt separated. The free acids obtained from these zinc salts weighed 7 grams and 6 grams respectively; they were light coloured oils which solidified partially after long standing. The acid recovered in the usual way from the filtrate from the zinc salts weighed 28 grams, and when heated again in exactly the same manner with calcium chloride and zinc chloride, it yielded no calcium salt, although appreciable quantities of the zinc salts were obtained.

All the semi-solid residues of the acids obtained by decomposing the zinc salts were spread on porous porcelain until the oily mother liquor had been completely absorbed, when an almost colourless acid was obtained, which, after crystallisation from water, melted sharply at  $105^\circ$ .

Tiemann (*Ber.*, 1895, 28, 2153), by a similar process, obtained an acid melting at  $140^\circ$  from the acids formed in his experiments on the fusion of camphoric acid with caustic potash; this he found to be a mixture of ordinary *d*-camphoric acid and *d*-*cistrans*-camphoric acid. In our experiments, although we were unable to isolate an acid melting at  $140^\circ$ , it seemed possible that the acid of melting point  $105^\circ$  might still be a mixture of the two camphoric acids present in molecular proportions differing from those of Tiemann's substance, and in order to test this assumption, we treated the acid of melting point  $105^\circ$  by the method recommended by Aschan (*Ber.*, 1894, 27, 2003) for separating these isomeric camphoric acids.

The acid (5 grams) was treated in the cold with acetyl chloride (18 grams), the excess of chloride removed by aspirating dry air through the product, and the solid residue treated in the cold with dilute soda. If the original acid had been a mixture of *d*-camphoric acid and *d*-*cistrans*-camphoric acid, the former would have been converted into camphoric anhydride by the acetyl chloride, whereas the latter would have remained unattacked; on subsequently treating the product

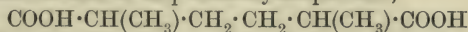
with cold soda, the camphoric anhydride would have remained undissolved. Our product, however, dissolved readily and completely, and on acidifying the alkaline solution with hydrochloric acid and extracting with ether, the acid melting at  $105^{\circ}$  was recovered. It cannot, therefore, be a mixture of isomeric camphoric acids.

This is an important experiment, as the analysis of the new acid shows that it differs from camphoric acid only in containing two additional hydrogen atoms, and we therefore propose to name it *dihydrocamphoric acid*. The following were the numbers found on analysis.

0.1316	gave	0.2874	CO <sub>2</sub>	and	0.1033	H <sub>2</sub> O.	C = 59.56 ;	H = 8.73.
0.1184	„	0.2574	CO <sub>2</sub>	„	0.0940	H <sub>2</sub> O.	C = 59.30 ;	H = 8.78.
0.1025	„	0.2230	CO <sub>2</sub>	„	0.0817	H <sub>2</sub> O.	C = 59.41 ;	H = 8.84.
C <sub>10</sub> H <sub>18</sub> O <sub>4</sub> requires C = 59.40 ; H = 8.91 per cent.								

This beautiful acid, when pure, melts at  $105\text{--}106^{\circ}$ ; it is sparingly soluble in cold water, readily in boiling water, and usually separates on cooling as an oil which, however, rapidly solidifies. It is readily soluble in alcohol, benzene, ethylic acetate, chloroform, and hot light petroleum, also in hot dilute formic acid (sp. gr. 1.06), separating from the latter on cooling, especially if the liquid is vigorously stirred, almost completely in curious nodular masses; formic acid of this strength is undoubtedly the best solvent from which to crystallise the acid, as its separation in the form of an oil is thus avoided.

Dihydrocamphoric acid is inactive; 1.2747 grams dissolved in 55 c.c. of alcohol gave no rotation in a 2 dem. tube of a Laurent's polarimeter. The dissociation constant for the electric conductivity of dihydrocamphoric acid was found by Dr. Ewan to be  $K = 0.00415$ ; this value is about the same as that of *aa*<sub>1</sub>-dimethyladipic acid,



( $K = 0.0042$ ), and nearly twice as large as that of camphoric acid ( $K = 0.0025$ ).

*Salts of Dihydrocamphoric Acid.*—The silver salt, C<sub>8</sub>H<sub>16</sub>(COOAg)<sub>2</sub>, which was prepared by precipitating a warm, slightly alkaline solution of the ammonium salt with silver nitrate, is an amorphous, very insoluble precipitate which, after washing with water and drying, gave the following results on analysis.

0.1132	gave	0.1210	CO <sub>2</sub> ,	0.0412	H <sub>2</sub> O	and	0.0583	Ag.	C = 29.15 ;
H = 4.05 ; Ag = 51.50.									

Additional silver determinations gave Ag = 51.74, 51.63, 51.82.

C<sub>8</sub>H<sub>16</sub>(COOAg)<sub>2</sub> requires C = 28.85 ; H = 3.85 ; Ag = 51.92 per cent.

*Oxidation of Dihydrocamphoric Acid.*

Dihydrocamphoric acid is only very slowly attacked by oxidising agents, and even after boiling with nitric acid for some time a considerable quantity of the acid may be recovered unchanged; potassium permanganate, moreover, is not decolorised by a cold solution of the acid in sodium carbonate even after half an hour. In order, if possible, to obtain some clue to the constitution of the acid, 2 grams were dissolved in dilute soda solution (containing 1 gram NaOH), a solution of 4 grams of permanganate added, the whole diluted to 250 c.c., and left for four weeks at the ordinary temperature, the procedure being exactly similar to that described by Balbiano (*Ber.*, 1892, 25, 640) in his experiments on the oxidation of camphoric acid to the acid  $C_9H_{16}O_6$ .

Oxidation took place very slowly, but at the end of four weeks nearly the whole of the permanganate had been decolorised; the last traces were destroyed by sodium hydrogen sulphite, and the whole was then heated to boiling, filtered, concentrated, acidified, and extracted with ether after saturation with ammonium sulphate. The residue obtained on distilling off the ether weighed nearly 2 grams, smelt strongly of acetic acid, and, on standing, deposited crystals which were found to consist of unchanged dihydrocamphoric acid. The precipitate, extracted with ether in a Soxhlet apparatus, yielded a small quantity of a viscid oil which appeared to contain a ketonic acid, since its solution in potash gave an immediate precipitate of bromoform with bromine; unfortunately, this oil did not give a characteristic semicarbazide or hydrazone, and its nature therefore could not be ascertained.

In order, if possible, to be in a position to carry out this experiment with larger quantities of dihydrocamphoric acid, we endeavoured to prepare it by fusing camphoric acid with potash in the presence of zinc dust, but although the conditions were varied greatly, we did not succeed in obtaining even a trace of the acid in this way.

*Anhydride of Dihydrocamphoric Acid and Formation of Dihydrocamphoketone,  $C_9H_{16}O$ .*

When dihydrocamphoric acid is rapidly heated in small quantities in a test tube, the greater portion sublimes unchanged, but the anhydride may be readily obtained by heating the pure acid (2 grams) with pure acetic anhydride (8 grams) in a reflux apparatus for about 15 minutes, and exposing the clear solution in a vacuum desiccator over solid potash and sulphuric acid for about 14 days until the odour of acetic anhydride has entirely disappeared. The gummy residue,



which could not be made to crystallise, gave results on analysis which agree approximately with those required for dihydrocamphoric anhydride.

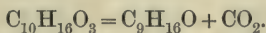
0.1530 gave 0.3629  $\text{CO}_2$  and 0.1194  $\text{H}_2\text{O}$ .  $\text{C} = 64.70$ ;  $\text{H} = 8.66$ .

0.1379 „ 0.3271  $\text{CO}_2$  „ 0.1073  $\text{H}_2\text{O}$ .  $\text{C} = 64.61$ ;  $\text{H} = 8.64$ .

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 65.22$ ;  $\text{H} = 8.69$  per cent.

This anhydride is only very slowly attacked by boiling water, but it dissolves in boiling potash solution, and, on acidifying the well-cooled alkaline solution, dihydrocamphoric acid is precipitated as an oil which rapidly solidifies, and then melts at  $103\text{--}104^\circ$ .

When heated to boiling at the ordinary pressure, the anhydride undergoes a very remarkable decomposition, carbonic anhydride being eliminated, and a new ketone,  $\text{C}_9\text{H}_{16}\text{O}$ , which we have called *dihydrocamphoketone*, formed,



In order to prepare this ketone in quantity sufficient for investigation, the anhydride obtained from 5 grams of dihydrocamphoric acid was heated to boiling in a small reflux apparatus for a few minutes, until carbon dioxide ceased to be evolved, and the residue was then distilled over completely. The distillate, which had a very penetrating odour of peppermint, was warmed with dilute potash solution for some time, and the insoluble oily ketone removed by means of ether; the alkaline solution, when acidified and extracted with ether in the usual way, yielded a small quantity (0.7 gram) of dihydrocamphoric acid, which had escaped decomposition.

The ethereal solution of the ketone after being washed with water, dried, and the ether distilled off, left nearly 4 grams of a residue, which on twice fractioning distilled almost constantly at  $180\text{--}181^\circ$  and gave the following numbers on analysis.

0.1336 gave 0.3761  $\text{CO}_2$  and 0.1343  $\text{H}_2\text{O}$ .  $\text{C} = 76.72$ ;  $\text{H} = 11.15$ .

0.1069 „ 0.3025  $\text{CO}_2$  „ 0.1099  $\text{H}_2\text{O}$ .  $\text{C} = 77.17$ ;  $\text{H} = 11.42$ .

$\text{C}_9\text{H}_{16}\text{O}$  requires  $\text{C} = 77.14$ ;  $\text{H} = 11.43$  per cent.

Dihydrocamphoketone is a volatile liquid having a very pronounced odour of peppermint; it combines readily with phenylhydrazine, hydroxylamine, and semicarbazide, the semicarbazone being the most characteristic derivative.

*Dihydrocamphoketone semicarbazone* was prepared by mixing the pure ketone with an excess of a saturated solution of semicarbazide hydrochloride, and adding a strong solution of sodium acetate and enough alcohol to make a clear solution; the liquid was then heated at  $80^\circ$  for 15 minutes and left overnight in the ice chest, when the semi-



carbazone separated almost completely in colourless needles. These, after being drained on a porous plate, washed with water and recrystallised from alcohol, were obtained as a white, sandy powder.

0.1231 gave 0.2728  $\text{CO}_2$  and 0.1122  $\text{H}_2\text{O}$ .  $\text{C} = 60.44$ ;  $\text{H} = 10.07$ .

0.1530 „ 27.8 c.c. moist nitrogen at  $17^\circ$  and 758 mm.  $\text{N} = 21.04$ .  
 $\text{C}_8\text{H}_{16}:\text{C}:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$  requires  $\text{C} = 60.91$ ;  $\text{H} = 9.65$ ;  $\text{N} = 21.32$  %.

The semicarbazone of dihydrocamphoketone, when moderately rapidly heated, melts at  $202\text{--}203^\circ$ , with incipient decomposition; it is almost insoluble in water and cold alcohol, and only sparingly soluble in boiling alcohol, so that it is necessary to use considerable quantities of this solvent in recrystallising it.

*Dihydrocamphoketoxime*,  $\text{C}_8\text{H}_{16}:\text{C}:\text{NOH}$ .—In order to prepare this, the pure ketone (2 grams) was dissolved in methylic alcohol, a concentrated aqueous solution of hydroxylamine hydrochloride (2.5 grams) added, and then a solution of potash (5 grams) in methylic alcohol. After two days, the methylic alcohol was removed by gently heating on the water bath, and the residue was diluted, acidified, and extracted with ether; this, after being washed and dried, left an oily residue, which, even after being kept for six days in a vacuum desiccator over sulphuric acid at  $0^\circ$ , did not show any signs of solidifying. It was analysed, with the following result.

0.1471 gave 12.5 c.c. moist nitrogen at  $16^\circ$  and 760 mm.  $\text{N} = 9.90$ .

$\text{C}_8\text{H}_{16}:\text{C}:\text{NOH}$  requires  $\text{N} = 9.03$  per cent.

Although these numbers do not agree so closely as might be desired, there can be no doubt that the substance is the oxime of dihydrocamphoketone, and many experiments were made (in the hope of being able to ascertain the constitution of the ketone) on the action of acetyl chloride and of sulphuric acid on the oxime, following Beckmann's directions, but without result. When mixed with acetyl chloride, a most violent deep crimson sticky mass, from which nothing definite could be isolated.

It was stated on page 23 that 8 grams of a neutral pungent oil, called A, were obtained when the fractions of the acids distilling between  $185$  and  $230^\circ$  (at 45 mm.) was treated with potash; on distillation, rather more than half of this passed over between  $175^\circ$  and  $195^\circ$  leaving, however, a considerable quantity of a dark brown residue of very high boiling point which was not further examined. The portion which distilled between  $175^\circ$  and  $195^\circ$ , on twice refractionating, yielded nearly 3 grams of a limpid oil boiling at  $179\text{--}181^\circ$  and smelling strongly of peppermint.

0.1611 gave 0.4538  $\text{CO}_2$  and 0.1660  $\text{H}_2\text{O}$ .  $\text{C} = 76.82$ ;  $\text{H} = 11.46$ .

0.1449 „ 0.4078  $\text{CO}_2$  „ 0.1465  $\text{H}_2\text{O}$ .  $\text{C} = 76.69$ ;  $\text{H} = 11.25$ .

$\text{C}_9\text{H}_{16}\text{O}$  requires  $\text{C} = 77.14$ ;  $\text{H} = 11.43$  per cent.

On careful examination, and especially by the preparation of the semi-carbazone melting at  $202\text{--}203^\circ$ , it was soon found that this oil was dihydrocamphoketone, and its formation in the manner explained is no doubt due to the partial decomposition of some of the anhydride of dihydrocamphoric acid, which must be present in the fraction of the anhydrides boiling at about  $180\text{--}230^\circ$  (45 mm.).

#### *Oxidation of Dihydrocamphoketone.*

This experiment was carried out as follows. About 50 c.c. of dilute nitric acid (sp. gr. 1.15) was heated to boiling in a flask into the neck of which a condenser had been ground, the flask was then removed from the sand-bath and 5 grams of the pure ketone added drop by drop through the condenser tube, when oxidation took place so vigorously that the liquid was kept boiling without external application of heat. When all the ketone had been added, the mixture was kept boiling for about half an hour, and then evaporated on a water bath, the residue being treated repeatedly with water to ensure the removal of all but the last traces of the nitric acid. Finally, the residue, which on standing overnight had deposited crystals, was dissolved in water, made slightly alkaline with ammonia, and boiled with an excess of calcium chloride solution. The filtrate from the precipitate of calcium oxalate thus formed was acidified, and the solution, after being saturated with ammonium sulphate, was extracted 25 times with pure ether. The ethereal solution, dried by calcium chloride and evaporated to a small bulk, was left for some days in a closed vessel at  $0^\circ$ , when crystals of succinic acid melting at  $183^\circ$  separated.

0.1278 gave 0.1914  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C} = 40.82$ ;  $\text{H} = 5.12$ .

$\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$  requires  $\text{C} = 40.68$ ;  $\text{H} = 5.10$  per cent.

The ethereal filtrate from the succinic acid was evaporated to dryness and the syrupy residue (2.6 grams), which did not crystallise even on long standing, was heated with excess of acetic anhydride for 1 hour. The acetic anhydride was then very slowly distilled off and the residue fractionated under reduced pressure, when nearly 2 grams passed over at  $160\text{--}170^\circ$  (35 mm.) as a moderately thick oil, which was insoluble in water, but dissolved slowly in hot potash solution: that is, it had the properties of an anhydride. The whole was now dissolved in a little pure benzene, the solution mixed with aniline (2 grams), and kept at  $0^\circ$  for 7 days in a closed vessel. The crystals

which had separated, after being left in contact with porous porcelain until quite colourless, were crystallised from dilute alcohol, by which means a substance melting at  $159^{\circ}$  was obtained.

0.0720 gave 3.5 c.c. moist nitrogen at  $17^{\circ}$  and 754 mm.  $N = 5.60$ .

$\text{COOH} \cdot \text{C}_6\text{H}_{12} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  requires  $N = 5.62$  per cent.

This anilic acid was heated for 1 hour in a sealed tube at  $140^{\circ}$  with 5 c.c. of a solution of hydrogen chloride in glacial acetic acid, and the product, after being allowed to evaporate to dryness over potash in a vacuum desiccator, was dissolved in a little water, saturated with ammonium sulphate, and extracted with ether in the usual way. The oil thus obtained rapidly and completely solidified, and on dissolving it in a few drops of water, saturating with hydrogen chloride, and allowing it to stand, it deposited colourless crystals; these were drained on porous porcelain and dried over potash in a desiccator, when they melted at  $94^{\circ}$ .

0.0875 gave 0.1760  $\text{CO}_2$  and 0.0661  $\text{H}_2\text{O}$ .  $C = 54.85$ ;  $H = 8.39$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $C = 55.18$ ;  $H = 8.04$  per cent.

The properties of this acid point to its being identical with the trimethylglutaric acid,  $\text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , which Balbiano (*Ber.*, 1895, 28, 1507) obtained from camphoric acid, as this acid melts at  $94$ — $95^{\circ}$  and gives an anilic acid melting at  $158$ — $159^{\circ}$ . Unfortunately, the quantity of our pure acid was not sufficient to allow of its being converted into the anhydride, as the melting point of this would have conclusively settled the question of the identity of the two acids.

#### FUSION OF CAMPHORIC ACID WITH CAUSTIC SODA.

In these experiments, 4 kilos. of camphoric acid were fused in quantities of 500 grams, with about eight times its weight of caustic soda, in a precisely similar manner and in the same apparatus as was used in the potash experiments. The slight differences in behaviour observed during the operation were the following.

1st. The action was apparently much more vigorous, and great care had to be taken in order to prevent the melt from frothing over.

2nd. The odour of menthol mentioned in the case of the caustic potash fusions was much more pronounced in this case.

3rd. The colour of the cold melt was pale brown.

4th. The whole operation lasted a somewhat shorter time, namely, from  $2\frac{1}{2}$ —3 hours, instead of from 3— $3\frac{1}{2}$ , as in the case of the fusion with potash.

*Working up of the Product.*—The process was carried out exactly as



described in the case of the potash melts (p. 11). The following numbers are of importance, as showing roughly the difference in behaviour of camphoric acid when fused with soda as compared with its behaviour with potash.

The weight of the sodium salts obtained by neutralisation and subsequent evaporation of the distillate from the steam distillation was  $1\frac{1}{2}$  kilos. (potash melts 4 kilos.), and the weight of free fatty acids obtained from the salts was 715 grams (potash melts 2.3 kilos.).

*Volatile Acids formed during the Fusion of Camphoric Acid with Soda.*

After a first rough fractionation giving the following numbers,

Fraction.	Weight in grams.
50—100°	71
100—125	13
125—135	10
135—150	207
above 150	360

the acids were dried over anhydrous sodium sulphate and frequently distilled, the process of drying being repeated after each distillation. The final numbers obtained were

Fraction.	Weight in grams.
50—100°	7
100—125	20
125—135	13
135—150	147
above 150	383

A few drops of the fraction 100—125°, when warmed with concentrated sulphuric acid, gave off a gas which burnt in air, and was probably carbon monoxide, produced by the decomposition of formic acid; but the amount was small.

The acids boiling above 150° yielded the following fractions.

Fraction.	Weight in grams.	Fraction.	Weight in grams.
below 150°	1	200—210°	33
150—160	1	210—220	42
160—170	16	220—230	46
170—180	38	230—240	71
180—190	51	above 240	52
190—200	35		

From the higher fractions, a small amount of solid matter separated which, from a determination of its melting point, was proved to be



pimelic (*iso*-propylsuccinic) acid. In order to remove this substance, the whole of the acids boiling above  $150^{\circ}$  were dissolved in ammonia, and subjected to steam distillation exactly in the same way as described in the purification of the acids from the potash melts (p. 13).

The accompanying table gives the results obtained after this treatment.

Fraction.	Weight in grams of acids before separation process was applied.	Weight in grams of acids after separation process was applied.	Weight in grams of oil got from the residual ammonium salts after steam distillation.
150—160°	1	5	}
160—170	16	18	
170—180	38	28	
180—190	51	16	}
190—200	35	29	
200—210	33	28	
210—220	42	21	}
220—230	46	30	
230—240	71	68	
above 240	52	13	}

The difference in the weights of the fractions of the fatty acids obtained from the potash and soda melts respectively is so marked that, for the sake of comparison, the following data are here inserted, the numbers given being the weights obtained after the distillation of the ammonium salts in steam. For this purpose, the weights have been put in percentages, calculated on the camphoric acid used, this being necessary owing to the fact that less camphoric acid was used in the soda than in the potash fusions; the most noticeable differences in the acids from the two melts are,

1st. The large amounts of the lower fractions in the potash melts as compared with the very small amounts of these fractions in the soda melts.

2nd. The comparatively large amount of the higher fractions, and in particular of the fraction 230—240°, in the “caustic soda” acids (see table, p. 33).

*Residue from the Steam Distillation.*—These residues were worked up as already described in the case of the potash melts (see p. 11). When the “crystalline residue from partial evaporation” was dissolved in acid, a thick, black scum (A) formed on the surface, which was separated by filtration; it weighed 185 grams. On extracting the filtrate with ether, 167 grams of a nearly colourless oil (B) was obtained.

Fraction.	Caustic Potash.	Caustic Soda.
	Percentage weight in grams after separation by means of ammonia.	Percentage weight in grams after separation by means of ammonia.
50—100°	0·00	0·17
100—125	14·02	0·50
125—135	6·60	0·30
135—150	5·70	3·70
150—160	0·62	0·10
160—170	0·50	0·40
170—180	0·50	0·70
180—190	0·70	0·40
190—200	0·40	0·70
200—210	0·86	0·70
210—220	0·60	0·50
220—230	1·08	0·70
230—240	0·40	1·70
above 240	0·12	0·30

The "residue from complete evaporation" gave 348 grams of a colourless oil (C).

*Volatile Acids Formed in the Fusion of Camphoric Acid with Soda.*

*The Fraction 100—125° contains Acetic Acid, CH<sub>3</sub>·COOH.*—The fractions 100—125° and 125—135° were dried in contact with concentrated sulphuric acid and refractionated in order to see whether any acetic acid could be obtained. After repeated distillation, during which most of the already small fractions passed over either below 100° or above 135°, 2·5 grams boiling between 116—120° were collected. On converting this liquid into the anilide, the product was proved to be acetanilide from its melting point and crystalline appearance.

*The Fraction 135—150° contains Propionic Acid, CH<sub>3</sub>·CH<sub>2</sub>·COOH.*—After repeated very careful fractionation with a column, an acid was isolated which distilled constantly at 140°, and was evidently propionic acid.

0·1530 gave 0·2731 CO<sub>2</sub> and 0·1156 H<sub>2</sub>O. C = 48·62; H = 8·36.

C<sub>3</sub>H<sub>6</sub>O<sub>2</sub> requires C = 48·64; H = 8·10 per cent.

The anilide of this acid was prepared by heating it with aniline and recrystallising the product from light petroleum (b. p. 100—120°); the white plates thus obtained were almost insoluble in water, more soluble in light petroleum, and very soluble in alcohol and ether. The substance melted at 103—104°.

0.2072 gave 16.8 c.c. moist nitrogen at 15° and 768 mm.  $N = 9.59$ .

$C_9H_{11}NO$  requires  $N = 9.39$  per cent.

The melting point of propionanilide as given by Sestini (*Zeitschrift für Chemie*, 1871, 35) is 92°, and by Kelbe (*Ber.*, 1883, 16, 1200) as 105°. A specimen of the anilide which we prepared from pure propionic acid and pure aniline melted at 103—104°, and was identical with the anilide obtained by us as described above.

*The Fraction 150—160° contains Isobutyric Acid*,  $CH(CH_3)_2 \cdot COOH$ . After repeated fractionation of all the acids boiling between 150—180°, it was found that the greater portion passed over between 150° and 160° (30 grams). Of this amount, all boiling between 153—157° was collected separately, and a portion boiling at 155° submitted to analysis, when numbers were obtained which indicated that the acid was *iso*-butyric acid, a result confirmed by the examination of its properties.

0.1112 gave 0.2210  $CO_2$  and 0.0914  $H_2O$ .  $C = 54.22$ ;  $H = 9.12$ .

$C_4H_8O_2$  requires  $C = 54.54$ ;  $H = 9.09$  per cent.

The anilide, prepared from this acid in the usual way, crystallised from light petroleum (b. p. 60—90°) in glistening, white needles, melting at 105°.

0.1058 gave 8 c.c. moist nitrogen at 12° and 754 mm.  $N = 8.90$ .

$C_{10}H_{13}NO$  requires  $N = 8.59$  per cent.

This anilide is insoluble in cold water, but melts under boiling water to an oil which crystallises on cooling. It is insoluble in cold light petroleum (b. p. 60—90°), but dissolves readily in chloroform, alcohol, ether and boiling light petroleum.

Norton (*Amer. Chem. J.*, 7, 117) describes the anilide of isobutyric acid as a substance easily soluble in hot water and melting at 102.5°. As the melting point and solubility in water of the anilide of the acid boiling at 153—157° did not agree with Norton's observations, some pure isobutyranilide was made from pure isobutyric acid. It crystallised from light petroleum (b. p. 60—90°) in colourless, feathery needles which melted at 105°; it was almost insoluble in boiling water, but melted to a colourless oil which solidified on cooling, and agreed in every respect with the properties of the anilide obtained from the acid boiling at 153—157°.

The *calcium salt* of this acid was prepared by boiling the purified acid with water and excess of calcium carbonate; on concentrating, the filtrate deposited colourless, glistening, feathery needles, which were collected, dried by exposure to air, and the water of crystallisation determined.

0.2012 lost 0.0518  $\text{H}_2\text{O}$  at  $155^\circ$ .  $\text{H}_2\text{O} = 25.74$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 25.17$  per cent.

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 29.60$  per cent.

This number is practically identical with the one obtained for calcium isobutyrate from the potash fusions (p. 15). A calcium determination in the dry salt was made.

0.1506 gave 0.0976  $\text{CaSO}_4$ .  $\text{Ca} = 19.05$ .

$(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}$  requires  $\text{Ca} = 18.69$  per cent.

It was pointed out in discussing the acids from the potash melts (p. 15) that the fraction  $150\text{--}170^\circ$  could, at the most, only contain traces of normal butyric acid: and it is interesting that, in the case of the acids from the soda melts, the same point is brought out, as, although *iso*-butyric acid was present in quantity, no butyric acid could be detected.

*The Investigation of the Acids from the Soda Melts boiling between  $200^\circ$  and  $250^\circ$ .*

This portion of the acids, which weighed about 160 grams, was ten times carefully fractionated, when the following fractions were obtained.

195—200° = 9 grams.	225—230° = 9 grams.
200—205 = 7 „	230—235 = 15 „
205—210 = 14 „	235—240 = 17 „
210—215 = 15 „	240—245 = 16 „
215—220 = 8 „	245—250 = 10 „
220—225 = 14 „	Residue = 4 „

The acids boiling between  $205^\circ$  and  $215^\circ$  were treated exactly in the same way as described in the case of the acids from the potash melts boiling at  $200\text{--}220^\circ$  (p. 18), and an anilide was obtained which melted at  $105^\circ$  and was sparingly soluble in light petroleum; on analysis, it gave the following results.

0.1140 gave 6.6 c.c. moist nitrogen at  $13^\circ$  and 770 mm.  $\text{N} = 6.93$ .

$\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$  requires  $\text{N} = 6.83$  per cent.

The anilide (8 grams) was decomposed by heating with hydrochloric acid, and the liberated fatty acid fractionated, when nearly the whole passed over at  $209\text{--}210^\circ$ , and, on analysis, gave the following result.

0.1351 gave 0.3194  $\text{CO}_2$  and 0.1304  $\text{H}_2\text{O}$ .  $\text{C} = 64.52$ ;  $\text{H} = 10.73$ .

$\text{C}_6\text{H}_{13}\cdot\text{COOH}$  requires  $\text{C} = 64.62$ .  $\text{H} = 10.77$  per cent.



The *silver salt*, prepared as usual, was analysed.

0.1197, on ignition, gave 0.0542 Ag.  $\text{Ag} = 45.28$ .

$\text{C}_6\text{H}_{13}\cdot\text{COOAg}$  requires  $\text{Ag} = 45.57$  per cent.

It is therefore clear that this acid, boiling at  $209\text{--}210^\circ$ , has the composition  $\text{C}_6\text{H}_{13}\cdot\text{COOH}$ , and as the boiling point of the acid, and the melting point and general proportion of its anilide, correspond exactly with those of the corresponding acid and anilide derived from the potash melts, there can scarcely be a doubt that the two acids are identical.

An examination of the table given at the head of this section would seem to indicate that a fatty acid boiling at  $225^\circ$  was present, but after repeated fractionation, the boiling point gradually rose, until ultimately the principal fraction came over at  $228\text{--}230^\circ$ . A small quantity boiling at  $229\text{--}230^\circ$ , collected for analysis, gave the following numbers.

0.1340 gave 0.3272  $\text{CO}_2$  and 0.1336  $\text{H}_2\text{O}$ .  $\text{C} = 66.59$ ;  $\text{H} = 11.08$ .

$\text{C}_7\text{H}_{15}\cdot\text{COOH}$  requires  $\text{C} = 66.66$ ;  $\text{H} = 11.11$  per cent.

It is very probable that this acid is the same as the acid boiling at  $230\text{--}232^\circ$  from the potash melts, but owing to the absence of characteristic derivatives, there appears to be little chance of determining either this point or the constitution of the acid.

Much more satisfactory results were obtained in examining the fraction of the acids boiling between  $235^\circ$  and  $250^\circ$ , and from this, on repeated fractionation, a considerable quantity of an acid was isolated, which boiled remarkably constantly at  $240\text{--}242^\circ$  and, on analysis, gave the following results.

0.1362 gave 0.3450  $\text{CO}_2$  and 0.1260  $\text{H}_2\text{O}$ .  $\text{C} = 69.01$ ;  $\text{H} = 10.28$ .

0.1100 „ 0.2775  $\text{CO}_2$  „ 0.1040  $\text{H}_2\text{O}$ .  $\text{C} = 68.73$ ;  $\text{H} = 10.50$ .

0.1232 „ 0.3104  $\text{CO}_2$  „ 0.1164  $\text{H}_2\text{O}$ .  $\text{C} = 68.71$ ;  $\text{H} = 10.49$ .

$\text{C}_9\text{H}_{16}\text{O}_2 = \text{C}_8\text{H}_{15}\cdot\text{COOH}$  requires  $\text{C} = 69.23$ ;  $\text{H} = 10.25$  per cent.

$\text{C}_9\text{H}_{18}\text{O}_2 = \text{C}_8\text{H}_{17}\cdot\text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.38$  per cent.

The *silver salt*, prepared in the usual way, and well washed with water, methylic alcohol, and ether was analysed.

0.2107 gave, on ignition, 0.0860 Ag.  $\text{Ag} = 40.81$

$\text{C}_8\text{H}_{15}\cdot\text{COOAg}$  requires  $\text{Ag} = 41.06$  per cent.

These analyses (those of the acid in particular) clearly show that the acid obtained from the soda melts and boiling at  $240\text{--}242^\circ$  is an unsaturated acid of the formula  $\text{C}_8\text{H}_{15}\cdot\text{COOH}$ ; in the case of the potash melts, however, the acid of this boiling point, although con-

taining traces of an unsaturated acid, has the formula  $C_8H_{17} \cdot COOH$ , and is a saturated acid. It will, however, be shown below that traces of the saturated acid,  $C_8H_{17} \cdot COOH$ , are present in the unsaturated acid from the soda melts, and this saturated acid is no doubt identical with that obtained from the potash melts.

The solution of the acid  $C_8H_{15} \cdot COOH$  in dilute soda reduces permanganate instantly in the cold, and also slowly decolorises a solution of bromine in chloroform. An attempt was made to prepare the dibromo-additive product of the acid, by exposing a weighed quantity to the action of dry bromine vapour in the dark, and then removing the excess of bromine by allowing the product to remain for some days over potash in a vacuum desiccator. It was found that 0.5017 gram of the oil had absorbed 0.6179 gram of bromine, corresponding with an increase in weight of 121 per cent., whereas on the assumption that a dibromo-acid of the formula  $C_8H_{15}Br_2 \cdot COOH$  had been formed in this process, the increase in weight should have been 115 per cent. An analysis of the crude product gave the following result.

0.2300 gave 0.2954 AgBr. Br = 54.34.

$C_8H_{15}Br_2 \cdot COOH$  requires Br = 50.63 per cent.

These somewhat high results are explained by the fact that, during the bromination, besides addition, a certain amount of substitution takes place, as was shown by the formation of some hydrogen bromide during the experiment; nevertheless, the results are interesting as confirming the unsaturated nature of the above acid.

*Oxidation of the Acid  $C_8H_{15} \cdot COOH$ .*—In order to obtain, if possible, some idea of the constitution of this acid, its behaviour towards oxidising agents was investigated, and a method was adopted which had been found to give valuable results in a somewhat analogous case, namely, the oxidation of the acid, first with alkaline potassium permanganate, and then with potassium dichromate and sulphuric acid.

Eleven grams of the acid boiling at 239—243° were dissolved in dilute sodium carbonate, the solution mixed with a large quantity of powdered ice in a circular porcelain pan, and the whole stirred with a turbine until the temperature had sunk to 0°. A rapid current of carbonic anhydride was now passed in, and then a cold saturated solution of permanganate run in drop by drop until the colour just remained permanent. The product was heated to boiling, and after filtering from the manganese precipitate, both filtrate and washings were evaporated to a small bulk. The concentrated solution was then heated to 70° in a large flask on a water bath, and a solution of potassium dichromate in dilute sulphuric acid run in in small quantities

at a time,\* until no further action seemed to take place; the whole was then saturated with ammonium sulphate and extracted 20 times with ether.

The ethereal solution on evaporation deposited a viscid, uninviting greenish oil, which did not solidify even on long standing; ultimately, however, a crystalline acid was isolated from it in the following way. The crude product, mixed with water, in which it only partially dissolved, was submitted to distillation with steam until oily drops ceased to come over; the residue in the distilling flask was then boiled with soda to precipitate any chromium present, filtered, the filtrate evaporated, acidified and again extracted with ether. The ethereal solution, after drying and evaporating, deposited a thick oil which, after being kept for some weeks at  $0^{\circ}$ , deposited about 1 gram of a solid acid, in the form of curious nodular masses. These crystals, after being freed from the oily mother liquor, by spreading the semi-solid mass on porous porcelain, were purified by recrystallisation from hydrochloric acid, when a perfectly colourless, crystalline acid melting at  $75^{\circ}$  was obtained.

0.1200 gave 0.2152  $\text{CO}_2$  and 0.0757  $\text{H}_2\text{O}$ .  $\text{C} = 48.86$ ;  $\text{H} = 7.00$ .

$\text{C}_6\text{H}_{10}\text{O}_4 = \text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$  requires  $\text{C} = 49.32$ ;  
 $\text{H} = 6.85$  per cent.

The remainder of the acid was converted into the anhydride by heating with acetyl chloride, and from this the anilic acid was prepared in the usual way, and recrystallised from dilute methylic alcohol. The glistening, crystalline mass thus obtained melted at  $113$ — $115^{\circ}$ , and showed all the properties of methylglutaric acid.

0.1238 gave 6.5 c.c. moist nitrogen at  $14^{\circ}$  and 765 mm.  $\text{N} = 6.20$ .

$\text{C}_{12}\text{H}_{15}\text{NO}_3$  requires  $\text{N} = 6.33$  per cent.

From these results, it appears that the unsaturated acid,  $\text{C}_8\text{H}_{15} \cdot \text{COOH}$ , when oxidised in the manner described above, yields  $\alpha$ -methylglutaric acid as one of its decomposition products.

The oily acid which had been separated from the methylglutaric acid by distillation with steam, as explained above, was extracted with ether and carefully fractionated, when nearly half a gram passed over at  $238$ — $244^{\circ}$ , very little product of a high or low boiling point being present.

The fraction which did not reduce permanganate in the cold was analysed.

0.1508 gave 0.3754  $\text{CO}_2$  and 0.1560  $\text{H}_2\text{O}$ .  $\text{C} = 67.87$ ;  $\text{H} = 11.47$ .

$\text{C}_8\text{H}_{17} \cdot \text{COOH}$  requires  $\text{C} = 68.35$ ;  $\text{H} = 11.39$  per cent.

\* During the early stages of this oxidation, the odour of acetone was distinctly noticeable.



There can be no doubt that this acid is identical with the acid,  $C_8H_{17}\cdot COOH$ , obtained from the potash melts and boiling at  $240-242^\circ$ , and this experiment shows that the unsaturated acid,  $C_8H_{15}\cdot COOH$ , from the soda melts contains traces of this saturated acid.

*Acids obtained from the Residues of the Steam Distillation. Pseudo-camphoric Acid,  $C_{10}H_{16}O_4$ .*

The first treatment of the residues of the steam distillation from the soda melts was described on page 33, and in subsequently working up the various products then obtained, the black scum A, weighing 185 grams, was first investigated. This uninviting looking mass was dissolved in ether, the ethereal solution washed with very dilute hydrochloric acid, dried over calcium chloride, and the ether distilled off; the residue, in quantities of 50 grams, was then heated with acetyl chloride (100 grams) for half an hour, the excess of the latter distilled off, and the oils thus obtained submitted to fractionation under a pressure of 46 mm., when nearly the whole passed over between  $200^\circ$  and  $210^\circ$ . This oily distillate, on being well shaken for some time with excess of a dilute solution of caustic soda, left a considerable portion undissolved; this was extracted with ether, and the ethereal solution dried and evaporated, when it deposited crystals of camphoric anhydride, which after recrystallisation from alcohol melted at  $218^\circ$ .

0.1022 gave 0.2468  $CO_2$  and 0.0718  $H_2O$ .  $C = 65.87$ ;  $H = 7.80$ .

$C_{10}H_{14}O_3$  requires  $C = 65.93$ ;  $H = 7.69$  per cent.

On dissolving the anhydride in hot potash solution and acidifying, ordinary *d*-camphoric acid was deposited; it melted at  $183-184^\circ$ , and, in alcoholic solution, had a rotatory power  $[\alpha]_D = +41^\circ$ .

The alkaline solution from which the camphoric anhydride had been removed by treatment with ether, was acidified with hydrochloric acid and extracted with ether, &c.; the oily product thus obtained deposited crystals which, after being purified by spreading them on porous porcelain and repeated recrystallisation from water, melted constantly at  $119-120^\circ$ , and gave the following results on analysis.

0.1208 gave 0.2648  $CO_2$  and 0.0890  $H_2O$ .  $C = 59.77$ ;  $H = 8.19$ .

0.1186 „ 0.2602  $CO_2$  „ 0.0844  $H_2O$ .  $C = 59.84$ ;  $H = 7.93$ .

0.1580 „ 0.3486  $CO_2$  „ 0.1149  $H_2O$ .  $C = 60.17$ ;  $H = 8.08$ .

$C_{10}H_{16}O_4$  requires  $C = 60.00$ ;  $H = 8.00$  per cent.

This very interesting acid is therefore isomeric with camphoric



acid, and for this reason we have called it *pseudocamphoric acid*. Pseudocamphoric acid is readily soluble in hot water, crystallising out, on cooling, in colourless, six-sided plates with bevelled edges, usually in stellate groups; it is also readily soluble in ether, alcohol, and benzene, but only sparingly in light petroleum. The solution of the acid in dilute sodium carbonate does not decolorise permanganate in the cold, and even on boiling oxidation takes place but very slowly.

*Salts of Pseudocamphoric Acid.*—The silver salt,  $C_8H_{14}(COOAg)_2$ , is obtained as a sparingly soluble, white precipitate on adding silver nitrate to a warm, slightly alkaline solution of the ammonium salt; after being well washed and dried at  $100^\circ$ , it was analysed.

0.2106 gave 0.2230  $CO_2$ , 0.0650  $H_2O$ , and 0.1094 Ag.

C = 28.91; H = 3.42; Ag = 51.94.

Additional silver determinations gave Ag = 51.76 and 51.86.

$C_8H_{14}(COOAg)_2$  requires C = 28.98; H = 3.38; Ag = 52.17 per cent.

The neutral solution of the ammonium salt of pseudocamphoric acid shows the following behaviour with reagents.

*Barium nitrate*, no precipitate.

*Copper sulphate*, a heavy, pale blue precipitate.

*Calcium chloride*, no precipitate in the cold, but on boiling, if the solution is moderately strong, the calcium salt separates as a white, crystalline precipitate.

*Lead acetate*, a heavy, white, very insoluble precipitate.

It was noticed during these experiments that, on evaporating a neutral solution of the ammonium salt in the water bath, it becomes strongly acid.

*Pseudocamphoric Anhydride*,  $C_8H_{14}\begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix}O$ .—In order to determine whether pseudocamphoric acid, like camphoric acid, was capable of forming an anhydride, the pure acid (2 grams) was heated with acetyl chloride (10 grams) in a reflux apparatus for 15 minutes, and the solution then allowed to remain over solid potash in a vacuum desiccator until the excess of acetyl chloride had been removed. The slightly yellowish residue, which quickly solidified, was left in contact with porous porcelain until colourless; it melted at  $52-53^\circ$  and, after recrystallisation from light petroleum, at  $53-54^\circ$ .

0.1524 gave 0.3664  $CO_2$  and 0.1066  $H_2O$ . C = 65.57; H = 7.77.

$C_{10}H_{14}O_3$  requires C = 65.93; H = 7.69 per cent.

Pseudocamphoric anhydride is readily soluble in the usual organic solvents, with the exception of light petroleum, in which it dissolves but sparingly. It distils without decomposition, and the distillate on

cooling at once solidifies to a colourless, crystalline mass melting at 52—53°.

*Pseudocamphoranilic Acid*,  $\text{COOH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .—When the solution of pseudocamphoric anhydride in benzene was mixed with aniline, the mixture became warm and after a time deposited a few crystals. As the quantity of these, however, was but small, the whole was heated in a basin on the water bath until free from benzene, and the residue mixed with ether and allowed to stand; the white, sparingly soluble substance which separated was collected, washed with ether, and purified by recrystallisation from dilute alcohol. The colourless, glistening, crystalline mass obtained in this way consisted of pure pseudocamphoranilic acid, as the following analysis shows.

0.2218 gave 10.3 c.c. nitrogen at 20° and 731 mm.  $\text{N} = 5.15$ .

$\text{C}_{16}\text{H}_{21}\text{NO}_3$  requires  $\text{N} = 5.09$  per cent.

When heated moderately rapidly in a capillary tube, pseudocamphoranilic acid melts at 208° without decomposition; it is almost insoluble in water, benzene, and light petroleum, but readily soluble in hot alcohol and acetone. When heated in a test tube, it decomposes at a high temperature, with elimination of water, the residue distilling as a colourless oil which solidifies on rubbing. Unfortunately, the amount of material at our disposal was too small to allow of the purification of this crude substance, which is doubtless the anil of pseudocamphoric acid.

#### *Action of Sulphuric Acid on Pseudocamphoric Acid.*

As camphoric acid when heated with sulphuric acid is converted into sulphocamphylic acid with evolution of carbon monoxide,  $\text{C}_{10}\text{H}_{16}\text{O}_4 + \text{H}_2\text{SO}_4 = \text{C}_9\text{H}_{14}\text{SO}_5 + \text{CO} + 2\text{H}_2\text{O}$ , it seemed interesting to determine whether pseudocamphoric acid, under similar conditions, would undergo an analogous decomposition.

In order to investigate this point, pure pseudocamphoric acid (0.5 gram) was mixed with concentrated sulphuric acid (3 c.c.) and the mixture heated at 100° in a test tube. The crystals soon dissolved and the solution, which at first was nearly colourless, rapidly became red and finally black; there was considerable effervescence, due to the evolution of carbon dioxide, and some sulphur dioxide, but no trace of carbon monoxide could be detected. As at the end of 10 minutes the effervescence had ceased, the whole was poured into ice-cold water, when it gave a brown solution in which a light brown, flocculent precipitate was suspended. This precipitate was collected,

but its nature could not be determined, as, although a sparingly soluble, colourless, crystalline substance resembling paraxylic acid was obtained from it, the amount was too small for analysis or further investigation. The filtrate from the brown precipitate was extracted several times with ether, and the ethereal solution, after washing and drying over calcium chloride, deposited, on evaporation, a slightly brownish oil, which dissolved readily in sodium carbonate; it could not, however, be obtained in a crystalline condition, and, therefore, was not analysed: it did not contain any sulphur. This experiment shows conclusively that pseudocamphoric acid, when treated with sulphuric acid, does not yield a sulphonic acid, and therefore behaves differently from camphoric acid.

#### *Oxidation of Pseudocamphoric Acid.*

This experiment need not be described in detail, as it was carried out under exactly the same conditions as the oxidation of dihydrocamphoric acid (p. 26), the quantities used being pseudocamphoric acid, 1·8 grams; caustic soda, 1 gram; and potassium permanganate, 4 grams; oxidation was nearly complete after 5 weeks at the ordinary temperature. The exchanged pseudocamphoric acid (0·6 gram) was isolated, and also 1·3 grams of a thick, yellow oil, which from its behaviour with bromine and potash and with phenylhydrazine evidently contained a ketonic acid, but as no crystalline derivative could be obtained its investigation was abandoned.

Returning to the investigations of the oils obtained from the residues of the steam distillation of the soda melts (p. 33), the two products B and C were mixed and treated with acetyl chloride, exactly as described in the case of the similar acids from the potash melts (p. 23). After distilling off the excess of acetyl chloride and fractionating under reduced pressure, the following fractions were collected.

150—175°	= 150 grams
175—200	} = 390 grams
200—240	

These fractions were treated separately with excess of dilute soda, the portion remaining insoluble being extracted with ether. The combined ethereal solutions, on evaporation, deposited an oil which solidified almost completely after a time; the crystals of *d*-camphoric anhydride thus obtained, after crystallisation, melted at 218—219°.

0·1140 gave 0·2745 CO<sub>2</sub> and 0·0769 H<sub>2</sub>O. C = 65·68; H = 7·50.

C<sub>10</sub>H<sub>14</sub>O<sub>8</sub> requires C = 65·93; H = 7·69 per cent.



The three alkaline extracts were also mixed, acidified with hydrochloric acid and extracted several times with ether; the residue left on evaporating the ethereal solution was dissolved in a slight excess of ammonia and boiled with calcium chloride, when a heavy, white precipitate of calcium pimelate (isopropylsuccinate) was formed. This, when decomposed by hydrochloric acid, gave large quantities of pimelic acid which, after recrystallisation from benzene, melted at 115—116°.

0.1008 gave 0.1940  $\text{CO}_2$  and 0.0678  $\text{H}_2\text{O}$ .  $\text{C} = 52.47$ ;  $\text{H} = 7.48$ .

$\text{C}_7\text{H}_{12}\text{O}_4$  requires  $\text{C} = 52.50$ ;  $\text{H} = 7.50$  per cent.

The filtrate from the calcium pimelate was treated, in the first instance, with zinc chloride exactly as described in the case of the potash melts (p. 24), but as the results were unsatisfactory, the following treatment was adopted. The concentrated solution of the ammonium salts, after acidifying, was extracted with ether in the usual way, and the thick oily product distilled under a pressure of 44 mm., collecting the fractions

165—210°; 210—235°; 235—260°.

The first of these, on standing, deposited crystals which, after crystallisation from water, melted at 117—119°, and were on analysis found to consist of pseudocamphoric acid.

On repeated fractionation, the combined fraction 210—260° yielded a considerable quantity of a very thick oil, which boiled remarkably constantly at 255—56° (50 mm.), and on analysis gave the following results.

0.1313 gave 0.2700  $\text{CO}_2$  and 0.0951  $\text{H}_2\text{O}$ .  $\text{C} = 56.09$ ;  $\text{H} = 8.04$ .

0.1293 gave 0.2645  $\text{CO}_2$  and 0.0960  $\text{H}_2\text{O}$ .  $\text{C} = 55.83$ ;  $\text{H} = 8.25$  per cent.

We were for a long time very much puzzled as to the nature of this acid, and it was only after numerous experiments, extending over a long period, that we were able to determine its composition.

In the first place, we found that the oil analysed, although boiling so constantly at 254—257° (50 mm.), was nevertheless not quite pure, as, when mixed with water, in which the bulk of the substance is excessively soluble, a small quantity remained undissolved, even after long shaking. In order to get rid of this impurity, the whole of the oil was shaken with water, filtered from the small quantity of undissolved oil, the filtrate evaporated to a small bulk on the water bath at a temperature of about 70°, and the residue allowed to stand over sulphuric acid in a vacuum until no further loss in weight occurred. Three analyses of the colourless, syrupy residue, obtained in two distinct experiments, gave the following numbers.



0.1007 gave 0.2110  $\text{CO}_2$  and 0.0748  $\text{H}_2\text{O}$ .  $\text{C}=57.14$ ;  $\text{H}=8.25$ .  
 0.1247 „ 0.2593  $\text{CO}_2$  „ 0.0938  $\text{H}_2\text{O}$ .  $\text{C}=56.71$ ;  $\text{H}=8.35$ .  
 0.1123 „ 0.2365  $\text{CO}_2$  „ 0.0853  $\text{H}_2\text{O}$ .  $\text{C}=57.44$ ;  $\text{H}=8.43$ .  
 $\text{C}_9\text{H}_{16}\text{O}_4$  requires  $\text{C}=57.45$ ;  $\text{H}=8.51$  per cent.

The *silver salt* of the acid, prepared by precipitating the slightly alkaline solution of the ammonium salt with silver nitrate, is a white, insoluble precipitate, which, after washing and drying at  $100^\circ$ , gave the following results on analysis.

0.2033 gave 0.2016  $\text{CO}_2$ , 0.0620  $\text{H}_2\text{O}$ , and 0.1090 Ag.

$\text{C}=27.04$ ;  $\text{H}=3.39$ ;  $\text{Ag}=53.61$ .

0.2070 gave 0.2094  $\text{CO}_2$ , 0.0635  $\text{H}_2\text{O}$  and 0.0112 Ag.

$\text{C}=27.58$ ;  $\text{H}=3.40$ ;  $\text{Ag}=53.72$ .

Additional silver determinations gave  $\text{Ag}=53.87$ ,  $53.58$ , and  $53.75$ .

$\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2$  requires  $\text{C}=26.86$ ;  $\text{H}=3.48$ ;  $\text{Ag}=53.73$  per cent.

The neutral solution of the ammonium salt of this acid shows the following behaviour with reagents.

*Barium chloride*, no precipitate, even on boiling.

*Calcium chloride*, with strong solutions, a white, gelatinous precipitate but this dissolves readily in water.

*Copper sulphate*, a bluish-green, gelatinous precipitate, which becomes caseous on warming.

*Lead acetate*, a heavy, white, amorphous precipitate.

The *anhydride* of the acid was prepared by boiling the acid with excess of acetic anhydride for two days in a reflux apparatus, and fractionating the product under reduced pressure (35 mm.); the colourless oil thus obtained, which was far less viscid than the acid, boiled at  $185-190^\circ$ .

0.1345 gave 0.3142  $\text{CO}_2$  and 0.0994  $\text{H}_2\text{O}$ .  $\text{C}=63.71$ ;  $\text{H}=8.21$ .

0.1872 „ 0.4368  $\text{CO}_2$  „ 0.1382  $\text{H}_2\text{O}$ .  $\text{C}=63.66$ ;  $\text{H}=8.20$ .

$\text{C}_9\text{H}_{14}\text{O}_3$  requires  $\text{C}=63.53$ ;  $\text{H}=8.24$  per cent.

From the results given above, it is clear that the oil distilling at  $254-257^\circ$  (50 mm.) is a mixture of a large quantity of an acid of the formula  $\text{C}_9\text{H}_{16}\text{O}_4$  with a small quantity of an oil the nature of which we were not able to determine. It is very remarkable that this acid, which is capable of forming an anhydride, should not do so at the high temperature at which it was distilled.

EXPERIMENTS ON THE SYNTHESIS OF CAMPHORIC  
ACID. PART I.

BY

WILLIAM HENRY BENTLEY

AND

WILLIAM HENRY PERKIN, JUN.

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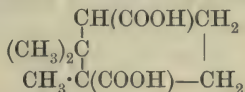
From the Transactions of the Chemical Society, 1898.



## Experiments on the Synthesis of Camphoric Acid. Part I.

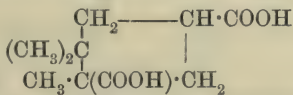
By WILLIAM HENRY BENTLEY and WILLIAM HENRY PERKIN, JUN.

DURING the course of a series of experiments on sulphocamphylic acid,  $\text{COOH} \cdot \text{C}_8\text{H}_{12} \cdot \text{SO}_3\text{H}$ , on which one of us has been engaged for a long time, many results have been obtained which are very difficult to understand if we assume that Bredt's formula for camphoric acid,



is correct.

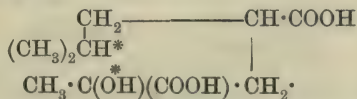
On the other hand, if this formula be slightly modified by altering the position of one of the carboxyl groups, so as to express the constitution of camphoric acid thus,



all the results obtained during the investigation on sulphocamphylic acid may be readily explained.

As, moreover, it appears that this formula is capable of accounting for all the other known reactions of camphoric acid, it seems highly probable that it may actually represent the constitution of camphoric acid.

In order, if possible, to decide this important point, experiments were made with the object of synthesising an acid of this constitution, the method adopted being to prepare, in the first place, an isobutylmethylhydroxyglutaric acid of the formula



and then to endeavour to remove the elements of water at the points \*\*. It seemed probable that this might be effected from the consideration that the elimination of water in this way would give rise to a 5 carbon ring—the ring which is supposed to be capable of the most ready formation, and also on account of the probability that camphoric acid, which is such an exceedingly stable substance, would be very likely to be produced if the conditions necessary for its formation presented themselves.

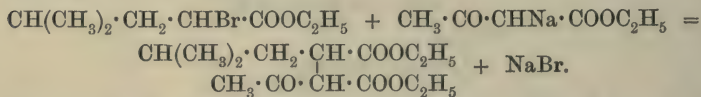
We have been successful in preparing isobutylmethylhydroxyglutaric



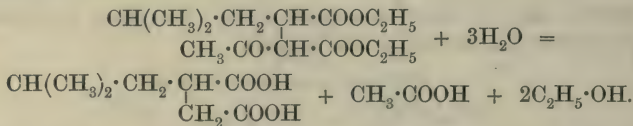
acid, but the elimination of water from this acid in the direction shown above has, so far, not been realised; it is to be hoped, however, that further experiments which are in progress may yet lead to the desired result.

The starting point in this investigation was isobutylacetic acid,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , which we prepared in considerable quantity in the usual way from ethylic isobutylmalonate by hydrolysis and subsequent distillation of the isobutylmalonic acid. When the product formed on treating this acid with phosphorus pentabromide and bromine was poured into alcohol, a very good yield of ethylic  $\alpha$ -bromisobutylacetate,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{COOC}_2\text{H}_5$ , was obtained as a colourless oil boiling at  $100\text{--}103^\circ$  (17mm.).

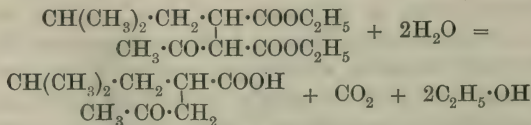
If now the sodium compound of ethylic acetoacetate be digested in alcoholic solution with this brominated ethereal salt, reaction takes place readily with elimination of sodium bromide, ethylic acetylisobutylsuccinate, a colourless oil boiling at  $160^\circ$  (25 mm.) being produced, according to the equation,



The hydrolysis of this ethereal salt by means of hydrochloric acid was next investigated, and after many experiments it was found that the course of the hydrolysis did not always go in the same direction, the nature of the products depending principally on the strength of the acid employed. If the hydrolysis is effected by boiling with dilute hydrochloric acid, the principal products of the reaction are isobutylsuccinic acid and acetic acid.

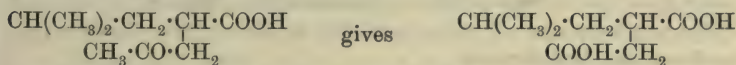


On the other hand, boiling with concentrated hydrochloric acid decomposes the ethereal salt in a different manner, isobutyllevulinic acid being produced.



Isobutyllevulinic acid, which is a viscid, odourless oil boiling at about  $190^\circ$  (30 mm.), shows all the properties of a ketonic acid, since, in ad-

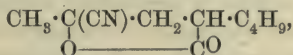
dition to dissolving in alkalis, it yields a well-defined *semicarbazone*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{C}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$ , melting at  $192^\circ$ . Its constitution is proved by the fact that when oxidised by bromine in the presence of potash, it gives an almost quantitative yield of isobutylsuccinic acid,



The next step was to investigate the action of hydrocyanic acid on isobutyllevulinic acid, and it was ultimately found that, if the conditions given in this paper are observed, addition readily takes place with formation of isobutylhydroxycyanovaleric acid.

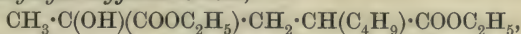


This hydroxycyanide is a crystalline substance which melts at  $95-96^\circ$ , and on distillation is decomposed with loss of water and formation of the corresponding lactone which melts at  $53^\circ$ ,

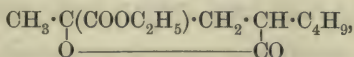


a behaviour which was to be expected, since the hydroxycyanide is at the same time a  $\gamma$ -hydroxy-acid.

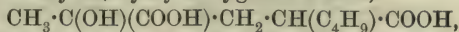
The hydrolysis of the hydroxycyanide was carried out by saturating its alcoholic solution with hydrogen chloride, and in this way an ethereal salt was obtained which was doubtless the ethereal salt of *isobutylmethylhydroxyglutaric acid*,



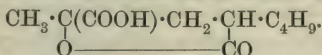
but if this ethereal salt be distilled under reduced pressure (17 mm.), an oil passes over at  $168^\circ$  which, on analysis, proved to be the ethylic salt of the lactone of isobutylmethylhydroxyglutaric acid,



alcohol having been eliminated during the distillation. From the ethylic salt, isobutylmethylhydroxyglutaric acid,



is readily obtained by hydrolysing it with alcoholic potash and precipitating the cold solution with hydrochloric acid; it is a beautifully crystalline substance which melts at  $134^\circ$  with elimination of water and formation of the lactone,



The latter, which is best prepared by treating the hydroxydibasic acid with acetyl chloride, is crystalline, and melts at about  $80^\circ$ . When dissolved in potash, it is converted into the potassium salt of the

hydroxy-acid, and this, on acidifying in the cold, yields the free acid, showing that this  $\gamma$ -hydroxy-acid is not so readily converted into its lactone as is the case with most  $\gamma$ -hydroxy-acids.

The following experiments were instituted in order, if possible, to obtain either camphoric acid or an isomeride by the elimination of water from isobutylmethylhydroxyglutaric acid in the manner indicated at the commencement of this paper, but so far we have been unable to obtain the desired result.

I. The diethylic salt of the acid, prepared from the silver salt by the action of ethylic iodide, was distilled under the ordinary pressure, when the whole passed over at  $290^{\circ}$  as a colourless oil; this, on analysis, was found to consist of the ethylic salt of the lactone of the hydroxy-acid, alcohol having been eliminated during the operation.

II. The diethylic salt was left in contact with excess of phosphorus pentoxide for eight days, and the product, after extraction with ether, was fractionated under the ordinary pressures; in this case, also, the distillate was found to consist of the ethylic salt of the lactone acid.

III. In order, if possible, to prevent the formation of the lactone, the hydroxy-dibasic acid was fused with potash at about  $300^{\circ}$ , at which temperature camphoric acid, if formed, would remain unattacked. It was, however, found that, during this experiment, the hydroxy-acid had been completely decomposed, isobutylsuccinic acid being produced.

IV. The carefully dried silver salt of the hydroxy-dibasic acid was submitted to distillation under reduced pressure. An oily distillate was obtained which, on refractionation, gave a large quantity of a fraction  $220-222^{\circ}$  (30 mm.); this, which solidified on standing, was found to be the lactone of the hydroxy-acid.

Several other substances of interest which were obtained during the course of this investigation are described in this paper.

*Isobutylacetic Acid*,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ .

This acid has already been prepared synthetically by the hydrolysis of isoamylic cyanide with alkalis (Frankland, Kolbe, *Annalen*, 65, 303), and also by the hydrolysis of ethylic isobutylacetoacetate with baryta (Rohn, *Annalen*, 1878, 190, 316); the isobutylacetic acid which was employed in this research was prepared from isobutylmalonic acid, a method which does not appear to have been described, and which we found to yield the acid in a very pure state.

Ethylic isobutylmalonate was prepared in the usual way by treating ethylic sodiomalonate with isobutylic bromide (compare Guthzeit, *Annalen*, 1881, 209, 236), and after careful fractionation\* the pure

\* During the fractionation, a small quantity of an oil of high boiling point, ethylic di-isobutyl malonate (see p. 61), is always obtained.



ethereal salt was hydrolysed by boiling with excess of alcoholic potash for four hours. After being mixed with water and freed from alcohol by evaporation, the residue was dissolved in a little water, acidified, and extracted six times with pure ether; the ethereal solution was then dried over calcium chloride, evaporated, and the residual crude isobutylmalonic acid decomposed by distillation. In this way, about 70 per cent. of the theoretical yield of pure isobutylacetic acid was readily obtained as a colourless, disagreeably-smelling oil boiling constantly at 200—201°.

0.1840 gave 0.4191  $\text{CO}_2$  and 0.1738  $\text{H}_2\text{O}$ .  $\text{C} = 62.12$ ;  $\text{H} = 10.48$ .

$\text{C}_5\text{H}_{11}\cdot\text{COOH}$  requires  $\text{C} = 62.07$ ;  $\text{H} = 10.35$  per cent.

*Ethylic Bromisobutylacetate*,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{COOC}_2\text{H}_5$ .—In order to prepare this, isobutylacetic acid (85 grams) was mixed with phosphorus pentabromide (127 grams), and after some time dry bromine (140 grams) was added in small quantities at a time, and the mixture heated at 50° for about 2 hours, until the evolution of hydrogen bromide had nearly ceased; the temperature was then raised to 100° in order to drive off the last traces of bromine. When cold, the product was poured into alcohol and the whole allowed to stand overnight. A large quantity of water was then added, the heavy oil which was precipitated was extracted with ether, and the ethereal solution, after being washed with sodium carbonate solution and with water, was dried; the ether was then distilled off, and the oily residue fractionated under reduced pressure. Pure ethylic bromisobutylacetate is thus readily obtained as a heavy, colourless, pleasant-smelling oil which boils at 100—103° (17 mm.) and has properties similar to other ethereal salts of  $\alpha$ -bromo-fatty acids. The yield is about 90 per cent. of the theoretical.

0.1522 gave 0.1280  $\text{AgBr}$ .  $\text{Br} = 35.78$ .

$\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{COOC}_2\text{H}_5$  requires  $\text{Br} = 35.87$  per cent.

*Ethylic Acetylisobutylsuccinate*,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\underset{\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5}{\text{CH}}\cdot\text{COOC}_2\text{H}_5$ .

This is produced by the interaction of ethylic  $\alpha$ -bromisobutylacetate with ethylic sodacetoacetate, as explained in the introduction of this paper. Sodium (11.5 grams) was dissolved in alcohol (130 grams), the solution mixed with ethylic acetoacetate (65 grams), ethylic bromisobutyl acetate (112 grams) added, and the mixture heated for 12—15 hours in a reflux apparatus on the water bath. The product, when cold, was mixed with water and extracted with ether, &c., the residue being fractionated under reduced pressure (25 mm.). The ethylic acetylisobutylsuccinate commences to distil at 140°, almost the whole



passing over between  $140^{\circ}$  and  $180^{\circ}$ ; a small quantity of oil boiling at  $200$ — $230^{\circ}$  was, however, obtained in each case, but this was not examined.

The fraction boiling at  $140$ — $180^{\circ}$  varies from 65—70 per cent. of the theoretical; a small portion of this, which was specially collected, distilled at about  $160^{\circ}$  (25 mm.) and gave the following numbers on analysis.

0.1188 gave 0.2660  $\text{CO}_2$  and 0.0935  $\text{H}_2\text{O}$ .  $\text{C} = 61.06$ ;  $\text{H} = 8.74$ .

Ethylis acetylisobutylsuccinate requires  $\text{C} = 61.76$ ;  $\text{H} = 8.82$  per cent.

Other analyses gave a similar result, and it was subsequently ascertained that the somewhat low numbers found were due to the substance containing traces of bromine (see p. 65).

*Hydrolysis of Ethylis Acetylisobutylsuccinate. Formation of Isobutylsuccinic Acid,* 
$$\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CH}_2 \cdot \text{COOH}}{\underset{|}{\text{CH}}} \cdot \text{COOH}$$
*and of  $\alpha$ -Isobutyllevulinic Acid,* 
$$\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2}{\underset{|}{\text{CH}}} \cdot \text{COOH}$$

a. The hydrolysis of ethylis acetylisobutylsuccinate with dilute hydrochloric acid yields *isobutylsuccinic acid*.

The fraction of the ethereal salt boiling at about  $150$ — $155^{\circ}$  (20 mm.) and weighing 48 grams was digested for about 15 hours in a reflux apparatus with 220 grams of dilute hydrochloric acid (1 acid: 2 of water), but even after boiling for this length of time, comparatively little of the ethereal salt had been hydrolysed. The liquid was accordingly extracted several times with ether, and the ethereal solution repeatedly shaken with small quantities of sodium carbonate; the aqueous solution, after being separated from the ether, was acidified and again extracted with ether. This second ethereal solution, after being dried and evaporated, left a yellowish oil which soon solidified. The crude crystalline mass, after being left in contact with porous porcelain, was purified by crystallisation from water, when it separated in colourless prisms which melted at  $109^{\circ}$ , and gave off water at about  $150^{\circ}$ .

0.1172 gave 0.2368  $\text{CO}_2$  and 0.0854  $\text{H}_2\text{O}$ .  $\text{C} = 55.10$ ;  $\text{H} = 8.09$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

It seemed likely that this acid was isobutylsuccinic acid, identical with the acid which Demarçay (*Ann. Chim. Ph.*, [v], 20, 492) obtained by the reduction of isobutylfumaric acid, and for which he gives the melting point  $103$ — $104^{\circ}$ . As, however, it was important to be quite sure of the identity of our acid, we prepared isobutylsuccinic acid

by a method which left no doubt as to its constitution, namely, the action of ethylic monochloracetate on ethylic isobutylsodiummalonate; the acid prepared in this way melted at  $109^{\circ}$ , and has all the properties of that obtained by the hydrolysis of ethylic acetylisobutylsuccinate.

The *anilic acid*,  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5}{\text{CH}} \cdot \text{COOH}$  (1), was prepared from both specimens by the following method. The acid (1 gram) was heated with a few grams of acetyl chloride for half an hour, the liquid placed over solid potash in a vacuum desiccator until the excess of acetyl chloride had been removed, and the oily residue dissolved in a little benzene and mixed with aniline (1 gram); the crystals which soon separated on standing were collected, dried on a porous plate, and purified by crystallisation from benzene mixed with a little alcohol; the isobutylsuccinanilic acid was thus obtained in glistening plates melting at  $138\text{--}139^{\circ}$ .

0.1792 gave 9.1 c.c. nitrogen at  $17^{\circ}$  and 745 mm.  $N = 5.82$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $N = 5.62$  per cent.

The same anilic acid was obtained from both preparations of isobutylsuccinic acid; subsequently it was also discovered that isobutylsuccinic acid is formed when ethylic acetylisobutylsuccinate is hydrolysed by heating it with a mixture of sulphuric acid, acetic acid, and a little water.

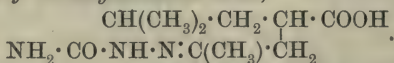
b. The hydrolysis of ethylic acetylisobutylsuccinate with strong hydrochloric acid results mainly in the formation of *isobutyllevulinic acid*. After numerous experiments had been tried in order to ascertain the most favourable conditions for the formation of isobutyllevulinic acid, the following method was adopted. Ethylic acetylisobutylsuccinate was digested in a reflux apparatus with about four times its volume of concentrated hydrochloric acid for 10 hours, but a portion only of the ethereal salt was hydrolysed. The product was shaken several times with ether, and the isobutyllevulinic acid separated from the unchanged ethereal salt, by extracting the ethereal solution with strong sodium carbonate solution, the ethylic salt recovered from the ethereal solution by evaporation being again submitted to hydrolysis as before; these operations were repeated until the concentrated hydrochloric acid had no further action on the oily layer (see p. 65). The combined sodium carbonate extracts were then acidified and extracted repeatedly with ether, &c., and the oil thus obtained was purified by distillation under reduced pressure; almost the whole distilled between  $160^{\circ}$  and  $180^{\circ}$  (20 mm.), and consisted for the most part of the ketonic acid, as the following analysis shows.

0.101 gave 0.2278  $\text{CO}_2$  and 0.0770  $\text{H}_2\text{O}$ .  $C = 61.51$ ;  $H = 8.47$ .

Isobutyllevulinic acid,  $\text{C}_9\text{H}_{16}\text{O}_3$ , requires  $C = 62.79$ ;  $H = 9.30$  per cent.

From this crude product, pure isobutyllevulinic acid may be readily obtained by converting it into the semicarbazone, purifying this, and subsequently decomposing the pure semicarbazone by means of hydrochloric acid.

*Semicarbazone of Isobutyllevulinic Acid,*



—This is readily prepared by adding the crude ketonic acid (30 grams), dissolved in a little alcohol, to a strong solution of semicarbazide hydrochloride (20 grams) and sodium acetate (32 grams), stirring the mixture vigorously, and heating to boiling for a few minutes; on cooling, a crystalline mass separates, which is collected, dried on a porous plate, and recrystallised from 70 per cent. alcohol; it is thus obtained in glistening plates melting at 192° with decomposition.

0.1594 gave 25.4 c.c. nitrogen at 16° and 762 mm.  $N = 18.63$ .

$\text{C}_{10}\text{H}_{19}\text{N}_3\text{O}_3$  requires  $N = 18.34$  per cent.

The semicarbazone of isobutyllevulinic acid is almost insoluble in water, benzene, and light petroleum, but dissolves readily in alcohol and in acetic acid. It is readily decomposed by hydrochloric acid into semicarbazide hydrochloride and isobutyllevulinic acid.

The pure semicarbazone (20 grams) was heated on the water bath with hydrochloric acid (30 c.c. of sp. gr. 1.1) and water (30 c.c.) until the crystals had been entirely decomposed and changed to an oil; the product was then extracted with ether in the usual way, and the oily residue fractionated under reduced pressure. The whole distilled at about 190° (30 mm.) as a colourless oil, consisting of pure isobutyllevulinic acid.

0.1150 gave 0.2646  $\text{CO}_2$  and 0.0964  $\text{H}_2\text{O}$ .  $C = 62.75$ ;  $H = 9.31$ .

$\text{C}_9\text{H}_{16}\text{O}_3$  requires  $C = 62.79$ ;  $H = 9.30$  per cent.

*Oxidation of Pure Isobutyllevulinic Acid by means of Potassium Hypobromite. Formation of Isobutylsuccinic Acid.*

It has already been pointed out (p. 50) that isobutylsuccinic acid is formed in considerable quantity during the hydrolysis, by means of dilute hydrochloric acid, of that portion of the product of the action of ethylic bromoisobutylacetate on ethylic sodacetoacetate which boils at 150—155° (20 mm.), and the formation of this acid proves that this oily product contains ethylic acetoisobutylsuccinate.

It seemed, however, quite likely that this oil might contain a second isomeric constituent formed by the elimination of hydrogen bromide from ethylic bromisobutylacetate, and the subsequent condensation of the ethylic  $\beta$ -isopropylacrylate  $\text{CH}(\text{CH}_3)_2 \cdot \text{CH} : \text{CH} \cdot \text{COOC}_2\text{H}_5$ ,



thus formed, with the ethylic acetoacetate, a series of reactions which have been repeatedly noticed in cases analogous to the above.

Since, then, it was possible that the substance we call isobutyllevulinic acid might have been derived from this second constituent, it became necessary, before using this acid for synthetical work, to be quite sure as to its constitution, and this was proved by oxidising the acid to isobutylsuccinic acid by means of potassium hypobromite.

Some of the ketonic acid which had been regenerated from the pure carbazone was dissolved in a considerable excess of strong potash solution and bromine added until, on standing for an hour, the solution liberated iodine from a solution of potassium iodide. The first drop of bromine produced a turbidity in the alkaline solution and then an oil separated which ultimately solidified; this, which consisted of carbon tetrabromide, was removed by filtration, the solution acidified with hydrochloric and sulphurous acids, and the oily acid extracted with ether. After distilling off the ether, an almost colourless oil was left, which showed no signs of solidifying; when, however, it had been dissolved in dilute sodium carbonate, the solution boiled with animal charcoal, filtered, and the filtrate acidified and allowed to stand for some days in a cold place, the acid was deposited in a semi-solid state, and in contact with porous porcelain became quite hard. After being purified by recrystallisation from water, pure isobutylsuccinic acid was obtained in colourless plates melting at  $109^{\circ}$ .

0.1364 gave 0.2748  $\text{CO}_2$  and 0.099  $\text{H}_2\text{O}$ .  $\text{C} = 54.95$ ;  $\text{H} = 8.06$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

The identity of this acid was further demonstrated by converting it into isobutylsuccinanilic acid and isobutylsuccinanil, which were found to be identical with the substances obtained from synthetical isobutylsuccinic acid (see p. 51).

*Action of Hydrogen Cyanide on  $\alpha$ -Isobutyllevulinic Acid. Formation of  $\alpha$ -Isobutyl- $\gamma\gamma$ -hydroxycyanovaleric Acid,*  
 $\text{CH}_3 \cdot \text{C}(\text{OH})(\text{CN}) \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{COOH}.$

In the first experiments on the action of hydrogen cyanide on isobutyllevulinic acid, the pure ketonic acid prepared from the semicarbazone was employed, and it was then found that this reaction gave rise to a solid hydroxycyanide and an oil containing much nitrogen; the latter was at first thought to be a stereoisomeric modification of the solid cyanide.

Subsequently, when it was found that it was unnecessary to employ such carefully purified ketonic acid, the usual method of procedure was as follows.



Isobutyllevulinic acid (b. p. 185—195° at 30 mm.), in quantities of 30 grams, was mixed with water (45 grams), and pure potassium cyanide (18 grams) added in small quantities at a time, the whole being cooled in a freezing mixture during the operation. The mixture, which soon became almost solid, was allowed to stand for about an hour, and concentrated hydrochloric acid (12 grams) then added, care being taken that the temperature did not rise much above 0°. After 2 hours, more hydrochloric acid (30 grams) was added, and the whole kept at 0° for about 20 hours. At the end of this time, it was seen that the oil which separated on adding the second quantity of hydrochloric acid had almost completely solidified; this semi-solid mass, after being washed and left in contact with porous porcelain until quite free from oily impurity, was recrystallised from dilute methylic alcohol, from which it separated in the form of beautiful, colourless needles melting at 95—96°. For analysis, the substance was dried over sulphuric acid in a vacuum, as it decomposes even below its melting point when heated in a water bath.

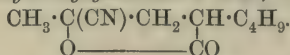
0.1220 gave 0.2484 CO<sub>2</sub> and 0.0980 H<sub>2</sub>O. C = 55.54; H = 8.92.

0.2356 „ 13.2 c.c. nitrogen at 14° and 764 mm. N = 6.63.

C<sub>10</sub>H<sub>17</sub>NO<sub>3</sub> + H<sub>2</sub>O requires C = 55.30; H = 8.75; N = 6.45 per cent.

Isobutylhydroxycyanovaleric acid appears, therefore, to crystallise from dilute methylic alcohol with 1H<sub>2</sub>O. It is readily soluble in acetic acid, alcohol and hot water, but only sparingly in benzene, chloroform or light petroleum; if warmed for some time with hot water, it decomposes, yielding hydrocyanic acid and an oil which is possibly regenerated isobutyllevulinic acid.

*Lactone of Isobutylhydroxycyanovaleric Acid,*



When pure isobutylhydroxycyanovaleric acid is distilled under reduced pressure (40 mm.), water is first eliminated, and then the temperature rises rapidly to 175°, nearly the whole of the residue distilling between 178° and 180° (40 mm.) as a colourless oil; this, however, is not the pure lactone, as is shown by the following analysis. Found, N = 5.75 per cent.; C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> requires N = 7.73 per cent.

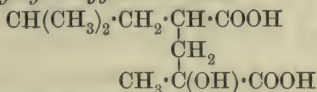
This oil, which appeared to contain some isobutyllevulinic acid, on long standing at 0°, deposited colourless plates which, after being spread on porous porcelain until quite dry and then washed with light petroleum, melted at 40—50°. The analysis now gave the correct numbers.

0.1550 gave 10.1 c.c. nitrogen at 22° and 760 mm.. N = 7.45.

C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> requires N = 7.73 per cent.

This substance, which is evidently the lactone of isobutylhydroxycyanovaleric acid, melts at  $53^{\circ}$ . It crystallises in beautiful, glistening plates, and is readily soluble in alcohol and ether, but almost insoluble in water. It is insoluble in cold soda solution, and when warmed the crystals melt and swim about in the hot alkaline solution as an oil.

*$\alpha$ -Isobutyl- $\alpha_1\alpha_1$ -methylhydroxyglutaric Acid.*



This acid is formed by the hydrolysis of isobutylhydroxycyanovaleric acid by means of hydrochloric acid, the method which was adopted for the hydrolysis and isolation of the acid being as follows. Absolute alcohol (60 grams) was saturated with dry hydrogen chloride, and to the cold liquid the solid cyano-acid (30 grams) was added, and the mixture then allowed to stand at the ordinary temperature for two days. At the end of this time, a considerable quantity of ammonium chloride had separated, and the process appeared to be complete; in order, however, to make sure that the whole of the cyano-acid had been hydrolysed, the product was heated on the water bath for 4 hours before being worked up. The whole was then cooled, diluted with water, and the oily ethereal salt which separated extracted with ether; this was washed, dried, and evaporated, and the oily residue purified by fractionation under reduced pressure. In this way, a colourless oil was obtained, which distilled almost constantly at  $168^{\circ}$  (17 mm.).

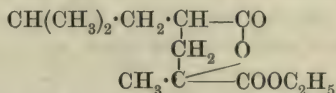
0.1152 gave 0.2666  $\text{CO}_2$  and 0.0930  $\text{H}_2\text{O}$ . C = 63.11; H = 8.97.

0.1080 „ 0.2502  $\text{CO}_2$  „ 0.0874  $\text{H}_2\text{O}$ . C = 63.18; H = 8.99 per cent.

$\text{C}_{12}\text{H}_{20}\text{O}_4$  requires C = 63.16; H = 8.77.

$\text{C}_{14}\text{H}_{26}\text{O}_5$  requires C = 61.31; H = 9.48 per cent.

This substance is therefore not the ethereal salt of isobutylmethylhydroxyglutaric acid itself ( $\text{C}_{14}\text{H}_{26}\text{O}_5$ ), but of the lactone of this acid ( $\text{C}_{12}\text{H}_{20}\text{O}_4$ ), that is, .



It is a colourless oil of faint odour, and distils without decomposition at about  $290^{\circ}$  under the ordinary pressures (see p. 57). In order to prepare the dibasic acid from this ethereal salt, the pure substance (25 grams) was added to a solution of potash (20 grams) in pure ethylic alcohol, and the solution heated in a reflux apparatus on the water

bath. In a short time, a solid potassium salt began to separate, which increased rapidly in quantity until the whole, after about an hour and a half, had become quite thick ; the mass was then cooled, the solid crystalline precipitate collected with the aid of the pump, washed with alcohol, and dried at  $100^{\circ}$ .

This substance, which proved to be the potassium salt of an organic acid, was dissolved in water, and the solution, after filtering, was cooled with ice and carefully acidified with hydrochloric acid, when a beautifully crystalline acid was precipitated ; this was collected, washed, dried, and analysed, with the following result.

0.1164 gave 0.2348  $\text{CO}_2$  and 0.0876  $\text{H}_2\text{O}$ .  $\text{C} = 55.01$  ;  $\text{H} = 8.36$ .

$\text{C}_{10}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 55.04$  ;  $\text{H} = 8.26$  per cent.

The *silver salt* of the acid precipitated from a neutral solution of the ammonium salt is a white, amorphous, very insoluble substance. On analysis, it gave the following result.

0.1008 gave 0.0508 Ag.  $\text{Ag} = 50.39$ .

$\text{C}_{10}\text{H}_{16}\text{Ag}_2\text{O}_5$  requires  $\text{Ag} = 50.00$  per cent.

These analyses prove that the acid obtained in this way is *isobutylmethylhydroxyglutaric acid*. When heated in a capillary tube, it softens at  $128^{\circ}$  and melts at  $134^{\circ}$  with evolution of gas, due, no doubt, to the elimination of water and formation of the lactone (p. 58). It is sparingly soluble in cold, but dissolves in warm water ; if the solution, however, be boiled, an oil separates, a change which is obviously due to lactone formation. The dibasic acid is sparingly soluble in cold benzene and light petroleum, but dissolves readily in alcohol and acetic acid. It may be obtained in a beautifully crystalline condition by dissolving it in much warm ether, distilling off the ether until crystals begin to separate, and then allowing the solution to stand, when the greater part of the acid separates in beautiful, glistening, silky plates.

*Ethylic Isobutylmethylhydroxyglutarate*,  $\text{OH} \cdot \text{C}_8\text{H}_{15}(\text{COOC}_2\text{H}_5)_2$ .—In order to prepare this, experiments were first tried on the action of hydrogen chloride on the alcoholic solution of the acid, but as the ethereal salt which was formed proved on investigation to be the ethylic salt of the lactonic acid, we were forced to make the ethylic salt of the dibasic acid from the silver salt by the action of ethylic iodide.

The dry silver salt of the dibasic acid (10 grams) was heated in a reflux apparatus with ethylic iodide (10 grams) and pure dry ether for 2 hours on the water bath ; the silver iodide was then filtered off, washed with ether, the ethereal solution evaporated, and the residual almost colourless oil left in a vacuum desiccator over sulphuric



acid for about a week. The analysis of the oil gave numbers showing that it was the ethereal salt of the dibasic acid.

0.148 gave 0.3297  $\text{CO}_2$  and 0.126  $\text{H}_2\text{O}$ .  $\text{C} = 60.72$ ;  $\text{H} = 9.46$ .

$\text{OH} \cdot \text{C}_8\text{H}_{15}(\text{COOC}_2\text{H}_5)_2$  requires  $\text{C} = 61.31$ ;  $\text{H} = 9.48$  per cent.

When this oil is distilled under the ordinary pressure, alcohol is eliminated and a colourless, oily ethereal salt distils remarkably constantly at  $290^\circ$  with scarcely any decomposition; this, on analysis, proved to be the ethylic salt of the lactonic acid.

0.1362 gave 0.3136  $\text{CO}_2$  and 0.1116  $\text{H}_2\text{O}$ .  $\text{C} = 62.79$ ;  $\text{H} = 9.10$ .

$\text{COOC}_2\text{H}_5 \cdot \text{C}_8\text{H}_{15} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{O}$  requires  $\text{C} = 63.16$ ;  $\text{H} = 8.77$  per cent.

This, after being hydrolysed by boiling with excess of potash or methylic alcohol, was diluted with water, evaporated to dryness, and the residue, dissolved in a little water, was cooled, and acidified, when the colourless crystalline hydroxydibasic acid was precipitated.

0.1280 gave 0.2572  $\text{CO}_2$  and 0.0960  $\text{H}_2\text{O}$ .  $\text{C} = 54.80$ ;  $\text{H} = 8.33$ .

$\text{C}_{10}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 55.04$ ;  $\text{H} = 8.26$  per cent.

In a preliminary experiment, in which less alkali was used, some of the ethereal salt on hydrolysis yielded a solid melting at  $78^\circ$ , which evidently consisted of the lactonic acid produced by direct hydrolysis.

*Action of Phosphorus Pentoxide on Ethylic Isobutylmethylhydroxyglutarate.*—As stated in the introduction, this experiment was instituted with the object of eliminating water from the ethereal salt, and of thus forming a closed chain, but the reaction evidently proceeds differently, alcohol being eliminated and the ethereal salt of the lactonic acid formed. The diethylic salt (5 grams) was mixed with a large excess of phosphorus pentoxide and allowed to stand in a desiccator over phosphorus pentoxide for 8 days; the gelatinous mass thus formed was then mixed with water, the oil which separated extracted with ether, the ethereal solution washed with sodium carbonate, dried over calcium chloride, and evaporated. The oily residue, after standing for 7 days over sulphuric acid in a vacuum desiccator, was analysed.

0.1434 gave 0.3356  $\text{CO}_2$  and 0.1196  $\text{H}_2\text{O}$ .  $\text{C} = 63.82$ ;  $\text{H} = 9.26$ .

On distillation under the ordinary pressure, nearly the whole passed over at  $290$ — $292^\circ$ , and on analysis and further examination it proved to be the ethylic salt of the lactonic acid.

0.1290 gave 0.2976  $\text{CO}_2$  and 0.1060  $\text{H}_2\text{O}$ .  $\text{C} = 62.91$ ;  $\text{H} = 9.13$ .

$\text{COOC}_2\text{H}_5 \cdot \text{C}_8\text{H}_{15} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{O}$  requires  $\text{C} = 63.16$ ;  $\text{H} = 8.77$  per cent.



From this ethereal salt, by hydrolysis, both the lactonic acid and the dibasic acid were obtained, and the latter was analysed.

0.1024 gave 0.2064  $\text{CO}_2$  and 0.0767  $\text{H}_2\text{O}$ .  $\text{C} = 54.97$ ;  $\text{H} = 8.33$ .

$\text{C}_{10}\text{H}_{18}\text{O}_5$  requires  $\text{C} = 55.04$ ;  $\text{H} = 8.26$  per cent.

There can therefore be no doubt that the oily ethereal salt was simply the ethereal salt of the lactonic acid.

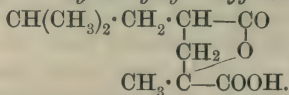
*Fusion of Isobutylmethylhydroxyglutaric Acid with Potash.*—This experiment was made in the hope that elimination of water might take place at the temperature of fusion with formation of a closed ring, which would probably be very stable, since camphoric acid itself is hardly attacked by fused potash at  $300^\circ$ . About 5 grams of the pure acid was fused with potash at  $220$ – $230^\circ$  for half an hour; the melt was then dissolved in water, and the clear solution acidified and extracted with ether. On evaporating the ether, an oil was left which, on standing for some days at  $0^\circ$ , gradually became nearly solid; it was then placed on porous porcelain and subsequently crystallised from water. The crystalline acid, melting at  $108$ – $109^\circ$ , thus obtained, proved to be isobutylsuccinic acid.

0.1219 gave 0.2472  $\text{CO}_2$  and 0.0892  $\text{H}_2\text{O}$ .  $\text{C} = 55.25$ ;  $\text{H} = 8.12$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

This experiment was repeated several times under different conditions, but isobutylsuccinic acid was formed in all cases.

*Lactone of Isobutylmethylhydroxyglutaric Acid,*



This lactone may be obtained from the hydroxydibasic acid in several ways, but we found that treating the acid with acetyl chloride yielded the best results. The pure hydroxydibasic acid boiled for a few minutes with a little pure acetyl chloride and then allowed to evaporate in a vacuum desiccator over solid potash, deposited prismatic crystals on standing overnight. These were collected, drained on a porous plate until quite dry, and then analysed without further purification.

0.1200 gave 0.2636  $\text{CO}_2$  and 0.0882  $\text{H}_2\text{O}$ .  $\text{C} = 59.91$ ;  $\text{H} = 8.16$ .

$\text{C}_{10}\text{H}_{16}\text{O}_4$  requires  $\text{C} = 60.00$ ;  $\text{H} = 8.00$  per cent.

The lactone of isobutylmethylhydroxyglutaric acid melts at about  $80^\circ$ , dissolves readily in alcohol and acetic acid, but is nearly insoluble in cold benzene, light petroleum, and water. When left in contact with water at about  $60^\circ$ , it gradually dissolves, probably with forma-

tion of the hydroxy-dibasic acid; in alkalis, it dissolves readily, and if the solutions are precipitated at once by hydrochloric acid, the lactone separates unchanged. If, however, the lactone is heated with excess of alkali for some time, and the solution then cooled with ice and cautiously acidified, the precipitate consists of the hydroxy-dibasic acid.

*Investigation of the Liquid Formed during the Action of Hydrogen Cyanide on Isobutyllevulinic Acid.*

It has already been stated that isobutyllevulinic acid reacts with hydrogen cyanide with formation of isobutylhydroxycyanovaleric acid, but the yield of the latter is not more than 50—60 per cent. of the theoretical, owing to the fact that some oily substance is always obtained at the same time; this is absorbed by the porous plates during the process of purification of the solid nitrile, and as it seemed possible that the examination of this oil might yield interesting results, these plates were broken up and extracted with ether in a Soxhlet apparatus. On distilling off the ether from the extract, a thick, dark brown oil containing nitrogen was left, and with this the following experiments were made.

*Behaviour of the Oil on Distillation.*—About one-third of the oil was distilled under reduced pressure (30 mm.), when, after a little water had come over, the temperature rose rapidly to  $140^{\circ}$ , most of the oil distilling at  $175$ — $185^{\circ}$ .

*Etherification of the Crude Oil.*—The crude, dark brown oil was dissolved in alcohol, the alcoholic solution saturated with hydrogen chloride, and the mixture left in the cold for two days, during which time a considerable quantity of ammonium chloride separated. The liquid was then heated in a reflux apparatus for one hour, diluted with water, and the oil which separated extracted with ether; the ethereal solution, after being washed with water and with sodium carbonate solution, dried over calcium chloride, and the ether distilled off, left an oil which was distilled under reduced pressure (25 mm.); almost the whole passed over between  $140^{\circ}$  and  $200^{\circ}$ , by far the larger portion at  $150$ — $160^{\circ}$ . The latter fraction gave the following results on analysis.

0.1170 gave 0.2810  $\text{CO}_2$  and 0.0992  $\text{H}_2\text{O}$ . C = 65.50; H = 9.41.

0.1285 „ 0.3102  $\text{CO}_2$  „ 0.1132  $\text{H}_2\text{O}$ . C = 65.84; H = 9.80.

Ethylisobutyllevulinate,  $\text{C}_{11}\text{H}_{20}\text{O}_3$ , requires C = 66.0; H = 10.0 p. cent.

As this oil on hydrolysis gave a liquid acid which, with semicarbazide hydrochloride yielded a semicarbazone melting approximately at  $185^{\circ}$ , there can be no doubt that it is ethylisobutyllevulinate, and this experiment shows that the original brown oil either contained

and extracted with pure ether. The ethereal solution, after being dried over calcium chloride and evaporated, gave an oily residue which solidified only very slowly, even when placed in a vacuum desiccator over sulphuric acid. After 14 days, the solid acid was pressed on porous plates in order to remove oily matter, and then purified by recrystallisation from light petroleum (b. p. 80—90°), when it was obtained in thick prisms melting at 145—150° with evolution of gas.

0.1054 gave 0.2352 CO<sub>2</sub> and 0.0884 H<sub>2</sub>O. C = 60.86; H = 9.32.

(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>C(COOH)<sub>2</sub> requires C = 61.11; H = 9.26 per cent.

Di-isobutylmalonic acid is almost insoluble in water and benzene, but dissolves readily in alcohol and in hot light petroleum (b. p. 80—90°); it is only sparingly soluble in cold light petroleum.

*Di-isobutylacetic Acid*, [CH(CH<sub>3</sub>)<sub>2</sub>·CH<sub>2</sub>]<sub>2</sub>CH·COOH, and its Derivatives.

In order to prepare this acid, crude di-isobutylmalonic acid was heated until carbon dioxide was no longer evolved, and it was then distilled. From the distillate, by fractional distillation, pure di-isobutylacetic acid was readily obtained as a viscid, colourless oil, of feeble odour, and boiling at 225—230° (730 mm.).

0.1004 gave 0.2560 CO<sub>2</sub> and 0.1050 H<sub>2</sub>O. C = 69.54; H = 11.61.

C<sub>10</sub>H<sub>20</sub>O<sub>2</sub> requires C = 69.77; H = 11.62 per cent.

*Di-isobutylacetyl chloride*, CH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>·COCl.—This was obtained by the action of phosphorus trichloride on di-isobutylacetic acid. The acid (9 grams) and the phosphorus trichloride (4 grams) were heated together for 10 minutes in an oil bath, the liquid was then decanted from the phosphorous acid, and distilled under reduced pressure. Di-isobutylacetyl chloride is a colourless, pungent-smelling liquid which boils at 95° (20 mm.); it was not analysed, but at once converted into the undermentioned derivatives.

*Di-isobutylacetanilide*, CH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>·CO·NH·C<sub>6</sub>H<sub>5</sub>.—This was prepared by dissolving the acid chloride (3 grams) in pure, dry ether, and adding aniline (5 grams) also dissolved in ether. After some time, water was added, the ethereal solution separated and washed with dilute hydrochloric acid until free from aniline, then with water, dried over calcium chloride, and the ether distilled off. The oil which was left slowly solidified, and after being spread on a porous plate to remove oily impurities, was crystallised from light petroleum (b. p. 100—120°). The pure substance was thus obtained in needles melting at 111°. Analysis,

0.1738 gave 9 c.c. nitrogen at 17° and 750 mm. N = 5.92.

CH(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>·CO·NH·C<sub>6</sub>H<sub>5</sub> requires 5.66 per cent.

Di-isobutylacetanilide dissolves in benzene, alcohol and hot light



petroleum (b. p. 100—120°), but is only sparingly soluble in cold light petroleum.

*Di-isobutylacetoparatoluidide*,  $\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , was prepared from the acid chloride and paratoluidine in precisely the same manner as the anilide; it crystallises from light petroleum (b. p. 100—120°) in prismatic needles, melts at 140—141°, and is sparingly soluble in cold light petroleum, but readily in alcohol, chloroform, and benzene.

0.2661 gave 12.6 c.c. nitrogen at 17° and 746 mm.  $N = 5.36$ .

$\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  requires  $N = 5.36$  per cent.

*Di-isobutylacetamide*,  $\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH}_2$ , was prepared by adding the acid chloride (3 grams) to concentrated aqueous ammonia (10 c.c.), allowing the mixture to stand for some time, and then extracting with ether; the ethereal solution, dried over potassium carbonate and evaporated, left an oil which slowly solidified. This was purified by crystallising it, first from petroleum boiling at 40—60°, and afterwards from petroleum of high boiling point (100—120°) mixed with a little alcohol, when it was obtained in minute needles melting at 120—121°.

0.1472 gave 10.8 c.c. N at 17° and 750 mm.  $N = 8.40$ .

$\text{CH}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH}_2$  requires  $N = 8.18$  per cent.

Di-isobutylacetamide is very soluble in alcohol, but almost insoluble in water, and, when pure, almost insoluble in petroleum of high boiling point.

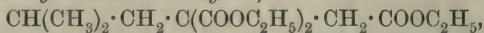
*Preparation of Isobutylsuccinic Acid,*  
 $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$ .

As this acid was needed for the purpose of comparison with the acid of the formula  $\text{C}_8\text{H}_{14}\text{O}_4$ , which had been obtained by the hydrolysis of ethylic acetylisobutylsuccinate as explained on p. 50, we prepared a considerable quantity of isobutylsuccinic acid by a process which has not been described before. Sodium (2 grams) was dissolved in absolute alcohol (24 grams), mixed with ethylic isobutylmalonate (25 grams), ethylic monochloracetate (14 grams) was added, and the mixture allowed to stand for some hours; it was then heated on the water bath for 4 hours, water was added, and the oil which separated extracted with ether. The ethereal solution, after being well washed with water, dried over calcium chloride and evaporated, left an oil which was purified by fractionation under reduced pressure. In this way a moderately good yield of a substance was obtained which distilled at 170—180° (25 mm.), and, on analysis, gave the following results.

0.1146 gave 0.2484  $\text{CO}_2$  and 0.0886  $\text{H}_2\text{O}$ .  $C = 59.11$ ;  $H = 8.58$ .

$\text{C}_{15}\text{H}_{26}\text{O}_6$  requires  $C = 59.60$ ;  $H = 8.60$  per cent.



*Ethylic isobutylethanetricarboxylate,*

is a colourless oil which, when distilled under ordinary pressures, appears to undergo but very little decomposition; on hydrolysis, it yields a solid, tribasic acid, which, when heated at  $180^\circ$ , loses carbon dioxide with formation of isobutylsuccinic acid.

The oily ethylic salt was hydrolysed with alcoholic potash in the usual way, the product evaporated until free from alcohol, acidified and repeatedly extracted with ether; after drying over calcium chloride and evaporating, the residual tribasic acid immediately solidified. This was not analysed, but at once converted into isobutylsuccinic acid by heating at  $180$ — $200^\circ$  until carbon dioxide ceased to be evolved; the crude product was then dissolved in hot water, filtered, and saturated with hydrogen chloride; on standing, a mass of crystals separated, which, after two recrystallisations from water, melted at  $109^\circ$ , and consisted of pure isobutylsuccinic acid.

0.1354 gave 0.2764  $\text{CO}_2$  and 0.1002  $\text{H}_2\text{O}$ .  $\text{C} = 55.67$ ;  $\text{H} = 8.22$ .

$\text{C}_8\text{H}_{14}\text{O}_4$  requires  $\text{C} = 55.17$ ;  $\text{H} = 8.04$  per cent.

*Isobutylsuccinanilic acid*,  $\text{C}_4\text{H}_9 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$  (?).

—In order to prepare this substance, the acid (2 grams) was digested with acetyl chloride for a few minutes, the excess of the latter removed by exposure over potash in a vacuum desiccator, and the residual liquid anhydride dissolved in a little benzene and mixed with aniline (1.5 grams). The solid matter which soon separated, after being drained on a porous plate and recrystallised from dilute alcohol, yielded the anilic acid in beautiful leaflets melting at  $138.5^\circ$ .

0.1818 gave 8.8 c.c. nitrogen at  $15^\circ$  and 558 mm.  $\text{N} = 5.66$ .

$\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires  $\text{N} = 5.62$  per cent.

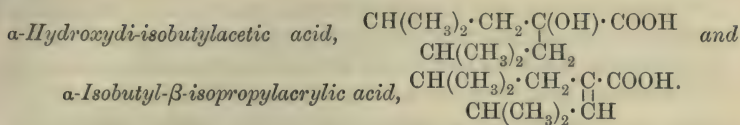
*Isobutylsuccinanil*,  $\text{C}_4\text{H}_9 \cdot \text{CH} \begin{array}{l} \text{—CO} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{array} \text{N} \cdot \text{C}_6\text{H}_5$ .—This was prepared by

heating the anilic acid at  $200^\circ$  for 5 minutes, and treating the gummy mass obtained with dilute ammonia, when it solidified immediately. This was ground up with dilute ammonia, collected, washed, and recrystallised from dilute alcohol.

0.1352 gave 7.1 c.c. nitrogen at  $16^\circ$  and 752 mm.  $\text{N} = 6.05$ .

$\text{C}_{14}\text{H}_{17}\text{NO}_2$  requires  $\text{N} = 6.06$  per cent.

*Isobutylsuccinanil* melts at  $109^\circ$ , and is readily soluble in alcohol and hot light petroleum, but only sparingly in cold light petroleum; it is almost insoluble in water and in dilute sodium carbonate solution.



In spite of the fact that the boiling point of ethylic acetylisobutylsuccinate (p. 50) is so constant, the numbers obtained on analysis were always nearly 1 per cent. low; this was subsequently found to be due to the fact that it contains traces of bromine. When this ethylic acetylisobutylsuccinate is hydrolysed with hydrochloric acid, there is always a small quantity of oil which remains unattacked, even after the treatment with hydrochloric acid has been repeated several times; in order to ascertain the nature of this oil, the small quantities from several operations were united and fractionated, when nearly the whole passed over at 138—140° (27 mm.), and on examination was found to contain bromine. The analysis of different samples gave the following results.

0.1365	gave	0.2649	CO <sub>2</sub>	and	0.1060	H <sub>2</sub> O.	C = 52.93 ; H = 8.63.
0.1705	„	0.3340	CO <sub>2</sub>	„	0.1320	H <sub>2</sub> O.	C = 53.43 ; H = 8.6.
0.1460	„	0.2880	CO <sub>2</sub>	„	0.1166	H <sub>2</sub> O.	C = 53.80 ; H = 8.87.
0.1214	„	0.2394	CO <sub>2</sub>	„	0.0936	H <sub>2</sub> O.	C = 53.78 ; H = 8.56.
0.2844	„	0.1748	AgBr.			Br = 26.15.	
0.2387	„	0.1502	AgBr.			Br = 26.77.	

These numbers agree with the formula  $\text{C}_{13}\text{H}_{25}\text{BrO}_2$ , which requires C = 53.2 ; H = 8.5 ; Br = 27.3 per cent.

A careful examination of this oil appears to us to prove that the true formula of the brominated ethylic salt is  $\text{C}_{12}\text{H}_{23}\text{BrO}_2$ , and that it is, in fact, *ethylic α-bromodi-isobutylacetate*,  $\text{C}(\text{C}_4\text{H}_9)_2\text{Br} \cdot \text{COOC}_2\text{H}_5$ . This formula requires C = 51.61 ; H = 8.24 ; Br. = 28.67 per cent., and the discrepancy between these and the numbers actually found was at first thought to be due to the possibility of some of the bromine having been replaced by chlorine during the prolonged boiling with hydrochloric acid. That this is not the case to any appreciable extent is shown by the fact that the 0.1502 gram of silver haloid obtained in one of the above analyses, after being reduced to silver, dissolved in nitric acid, and precipitated with hydrobromic acid, yielded 0.1478 gram of AgBr. Most probably the impurity in the brominated ethylic salt consists of traces of ethylic acetoisobutylsuccinate, which had escaped the hydrolysing action of the hydrochloric acid.

The presence of this brominated substance in the crude ethylic acetoisobutylsuccinate is explained by the fact that when the sodium compound of ethylic malonate is treated with isobutylic bromide, the

principal product is ethylic isobutylmalonate, but there is always formed at the same time some ethylic di-isobutylmalonate,  $C(C_4H_9)_2 \cdot (COOC_2H_5)_2$ .

This ethereal salt, on hydrolysis and subsequent elimination of carbon dioxide, yields di-isobutylacetic acid,  $CH(C_4H_9)_2 \cdot COOH$ , traces of which were evidently present in the isobutylacetic acid used in these experiments. In the subsequent bromination, this would be converted into  $\alpha$ -bromodi-isobutylacetic acid,  $CBBr(C_4H_9)_2 \cdot COOH$ , the ethylic salt of which is apparently not readily acted on by the sodium compound of ethylic acetoacetate, since it is found unchanged in the product of the reaction.

*Hydrolysis of Ethylic Di-isobutylbromacetate.*—When the brominated ethylic salt (12 grams) was digested in alcoholic solution with potash (15 grams) in a reflux apparatus, potassium bromide soon began to be deposited in crystals on the side of the flask. After boiling for 8 hours, the product was diluted with water, traces of a neutral oil removed by extraction with ether, and the aqueous solution evaporated with water until quite free from alcohol. The alkaline solution was then acidified, and the oily acid which separated was removed by treatment with ether. The ethereal solution, after drying over calcium chloride and evaporating, left a thick syrup which, on standing for some days over sulphuric acid in a vacuum-desiccator, gradually deposited hair-like crystals; these were collected with the aid of the pump, drained on a porous plate, and then recrystallised from light petroleum.

0.1243 gave 0.2890  $CO_2$  and 0.1206  $H_2O$ .  $C = 63.42$ ;  $H = 10.77$

$OH \cdot C(C_4H_9)_2 \cdot COOH$  requires  $C = 63.88$ ;  $H = 10.64$  per cent.

This beautifully crystalline substance melts at  $123-124^\circ$  and evidently consists of  *$\alpha$ -hydroxydi-isobutylacetic acid*; it is readily soluble in hot light petroleum (b. p.  $60-80^\circ$ ), sparingly so in the cold, and crystallises from this solvent in slender needles which, when dry, resemble cotton wool.

This acid is isomeric with  *$\alpha$ -isopropyl- $\beta$ -isobutylhydracrylic acid* (m. p.  $120^\circ$ ),  $CH(CH_3)_2 \cdot CH_2 \cdot CH(OH) \cdot CH(COOH) \cdot CH(CH_3)_2$ , which Wohlbrück (*Berichte*, 1887, 20, 2337) and Hantzsch (*Annalen*, 1888, 249, 65) obtained by the action of sodium on ethylic isovalerate.

The oily filtrate from the crude crystals of the  *$\alpha$ -hydroxydi-isobutylacetic acid* was fractionated under reduced pressure (35 mm.) when nearly the whole distilled constantly at  $153^\circ$ . The very thick, colourless syrup thus obtained gave the following results on analysis.

0.1793 gave 0.4569  $CO_2$  and 0.1725  $H_2O$ .  $C = 69.50$ ;  $H = 10.69$ .

$C_{10}H_{18}O_2$  requires  $C = 70.06$ ;  $H = 10.60$ .

This substance is evidently *isopropylisobutylacrylic acid*, and the fraction analysed may contain traces of hydroxydi-isobutylacetic acid,



which would account for the results of the above analysis being somewhat too low.

Isobutylisopropylacrylic acid distils without decomposition under the ordinary pressure at 240—241°. It is almost insoluble in water, but dissolves readily in dilute sodium carbonate solution, and this solution of the sodium salt rapidly decolorises permanganate, although, perhaps, not so readily as is usual with unsaturated acids.

Bromine is slowly decolorised by a solution of the acid in chloroform.

*Salts of Isobutylisopropylacrylic Acid.*—The ammonium salt of this acid dissociates on evaporating its solution on a water bath, ammonia being evolved, and the oily acid separating out. The *silver salt*,  $C_{10}H_{17}AgO_2$ , was obtained as a white, caseous precipitate on adding silver nitrate to a solution of the acid in a slight excess of ammonia; after washing well and drying first on a porous plate and then at 100° it was analysed.

0.2658 gave, on ignition, 0.1040 Ag. Ag = 39.12.

0.2555 " " " 0.0998 Ag. Ag = 39.06.

$C_{10}H_{17}AgO_2$  requires Ag = 38.99 per cent.

The neutral solution of the ammonium salt shows the following behaviour with reagents.

*Barium chloride*, no precipitate.

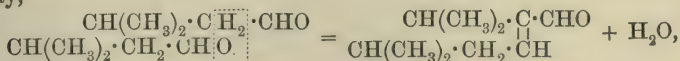
*Calcium chloride.*—If calcium chloride is added to a hot dilute solution of the ammonium salt, a beautifully crystalline characteristic calcium salt rapidly separates; this dissolves in much hot water, but does not appear to crystallise out again on cooling.

*Copper sulphate* gives a very insoluble bluish-green, caseous precipitate.

*Lead acetate*, a white caseous precipitate.

Isopropylisobutylacrylic acid is probably identical with the *amydecylenic acid* which Borodin (*Jahresbericht*, 1870, 680; *Berichte*, 1872, 5, 481) obtained by the oxidation of di-isovaleraldehyde,  $C_{10}H_{18}O$ , a substance which is produced when isovaleraldehyde is digested with potassium carbonate.

If we assume, as is probable, that in the formation of di-isovaleraldehyde two molecules of isovaleraldehyde condense in the following way,



then an aldehyde of this formula should, on oxidation, yield isopropylisobutylacrylic acid and, this appears to be the case, since amydecylenic acid is described by Borodin as an oil boiling at 241.5° without decomposition.



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# HOMOLOGUES OF BUTANETETRACARBOXYLIC ACID AND OF ADIPIC ACID.

BY

BEVAN LEAN, D.Sc., B.A.

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[From the Transactions of the Chemical Society, 1894.]

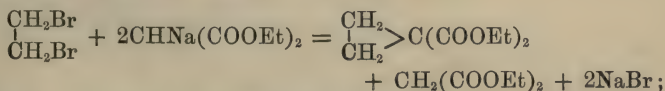


## Homologues of butanetetracarboxylic acid and of adipic acid.\*

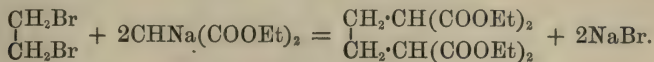
By BEVAN LEAN, D.Sc., B.A., Bishop Berkeley Fellow of Owens College.

### INTRODUCTION.

WHEN ethylene dibromide is treated with the monosodium derivative of ethylic malonate, the chief product is ethylic 1:1-trimethylenedicarboxylate (Perkin, Trans., 1887, 51, 1).



but, at the same time, an oil of high boiling-point is formed, which, however, constitutes only about 3 per cent. of the whole; this, on investigation, was found to be ethylic butanetetracarboxylate, and its formation may be represented by the equation—



The fact that this substance is produced in such small quantities made its further investigation a matter of very great difficulty; more recently, however, Professor W. H. Perkin, jun., has found that the substitution of ethylenic chloride for the bromide greatly increases the yield of ethylic butanetetracarboxylate. The method

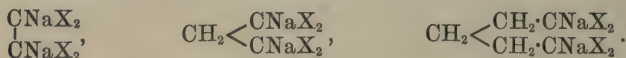
\* Part of a thesis accepted for the degree of Doctor of Science of the University of London.



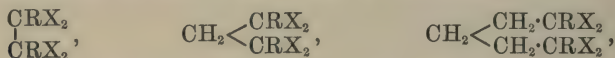
which is now adopted for the preparation of this substance is described in a paper published in this Journal (this vol., 578).

Ethylie butanetetracarboxylate, in constitution and properties, is very closely allied to the ethereal salts of ethane-, propane-, and pentane-tetracarboxylic acids, all of which have been investigated in detail.

These ethereal salts interact with sodium ethylate, forming disodium derivatives, the sodium displacing the hydrogen atoms of the two CH groups, and giving compounds, which, if X denote the group COOEt, may be represented thus—

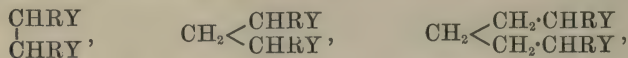


When these sodium derivatives are treated with alkylic haloïds disubstitution derivatives are formed of the general formulæ—



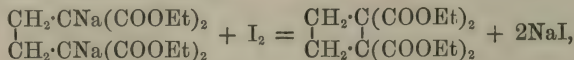
in which R represents an alkylic group, the action taking place readily, except in the case of the disodium derivative of ethylie ethane-tetracarboxylate, when it is necessary to heat the mixture at 150° (Guthzeit and Dressel, *Annalen*, **256**, 181; Perkin, *Trans.*, 1891, **59**, 818; Baeyer and Perkin, *Ber.*, **17**, 449).

On hydrolysis, these ethereal salts yield the corresponding tetracarboxylic acids, which lose 2 mols. of carbonic anhydride when heated at about 200°, and are converted into derivatives of succinic, glutaric and pimelic acids, of the general formulæ—



where Y represents the group COOH, just as ethylie ethane-, propane-, and pentane-tetracarboxylates, under similar circumstances, are converted into succinic, glutaric and pimelic acids respectively.

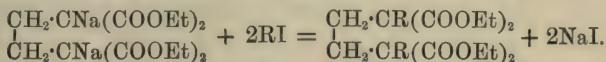
It has already been shown by Perkin (*loc. cit.*) that ethylie butane-tetracarboxylate is capable of forming a disodium derivative  $(\text{COOEt})_2\text{CNa} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CNa}(\text{COOEt})_2$ , and that this disodium derivative is converted by iodine into the ethereal salt of tetramethylenetetracarboxylic acid, thus—



but no further experiments could be instituted at that time with the disodium derivative, owing to the difficulty of obtaining sufficient of the ethereal salt. When, however, the method of preparation had been so improved as to make it possible to continue, in a satisfactory

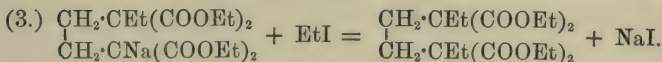
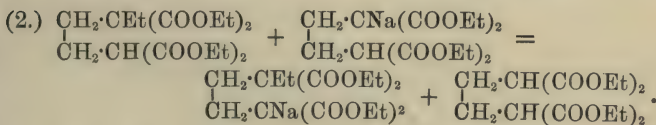
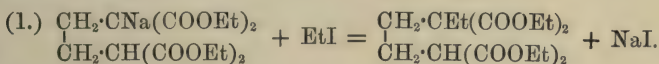
manner, the investigation of the substance, it was thought that interesting results would be obtained by studying the action of alkylic haloïds on the disodium derivative.

In carrying out this investigation, it was found that the disodium derivative of ethylic butanetetracarboxylate is readily acted on by alkylic iodides or chlorides, forming  $\alpha\alpha$ -dialkyl-substituted butanetetracarboxylic acid derivatives, thus—



The action takes place as soon as the substances are brought together, generally with considerable development of heat.

On the other hand, it has not been found possible to prepare monalkylic derivatives of butanetetracarboxylic acid by the action on ethylic butanetetracarboxylate of 1 mol. of sodium ethylate and 1 mol. of an alkylic haloïd. On attempting to prepare ethylic monethylbutanetetracarboxylate in this way, the product was found to consist of ethylic diethylbutanetetracarboxylate, one half of the ethylic butanetetracarboxylate being recovered as such. In explanation of this remarkable action, one must either suppose that ethylic butanetetracarboxylate is incapable of forming a monosodium derivative under such conditions, or that the decomposition of the monosodium derivative takes place thus—



Similarly, ethylic propanetetracarboxylate (Guthzeit and Dressel, *Annalen*, 256, 180, 188), and ethylic pentanetetracarboxylate (Perkin, *Trans.*, 1891, 59, 847), when treated with 1 mol. of sodium ethylate and an alkylic haloïd, yield, instead of a monalkylic derivative, a mixture of the dialkyl derivative with unchanged ethereal salt.

In the course of this investigation, a detailed study has been made of the dimethyl, diethyl, dicetyl, and dibenzyl derivatives of ethylic butanetetracarboxylate. They are all solids, and crystallise with considerable facility.

On hydrolysis, these ethereal salts yield the corresponding quadricarboxylic acids, which possess some very remarkable properties;

for, although they contain four carboxyl groups, they do not in all cases behave as quadribasic acids. When their basicity is determined by titration with standard solution of potassium hydrate, some of them act as bibasic acids; notably is this the case with dibenzylbutanetetracarboxylic acid, the result being the same whether phenolphthalein or litmus is used as the indicator. In this connection, it is to be noted that the silver and calcium salts of dibenzylbutanetetracarboxylic acid, which were obtained, were found to have the formulæ  $C_{22}H_{20}O_8Ag_2$  and  $C_{22}H_{20}O_8Ca + 2H_2O$  respectively. On the other hand, dimethyl-, diethyl-, and dicetyl-butane-tetracarboxylic acids, on being titrated with potassium hydrate, give different results, according as phenolphthalein or litmus is employed as indicator. They behave as quadribasic acids when phenolphthalein is used. If, however, one or two drops of litmus solution be added to the solution of these acids in potassium hydroxide, which has been rendered neutral to phenolphthalein by hydrochloric acid, a distinctly blue coloration is produced. On adding more hydrochloric acid, the blue coloration changes gradually to red, and the solution appears to become neutral to litmus only when sufficient hydrochloric acid is added to neutralise one half of the potassium hydroxide, which was equivalent, as shown by phenolphthalein, to the tetracarboxylic acid present. While the salts of dimethyl- and diethyl-butane-tetracarboxylic acid were quadribasic, those prepared in the same way from dicetylbutane-tetracarboxylic acid, like those of dibenzylbutane-tetracarboxylic acid, were found to be bibasic.\*

\* As regards the action of indicators, it has been shown that the quadribasic potassium salts of dimethyl-, diethyl-, and dicetyl-butane-tetracarboxylic acid are neutral to phenolphthalein but alkaline to litmus, and that, on titrating these acids, when using litmus as the indicator, the points of neutralisation are found to be very indefinite. Dibenzylbutane-tetracarboxylic acid, on the other hand, acts as a bibasic acid, both towards litmus and phenolphthalein. To illustrate further the difference in behaviour of indicators, reference may be made to a systematic investigation of the use of litmus, methyl-orange, and phenolphthalein as indicators, which was carried out by Smith in 1883 (*Chem. News*, 1883, 47, 136). The following table is compiled from his results.

	Oxalic.	Acetic.	Tartaric.	Citric.
Methyl-orange..	low results	very low results	very low results	very low results
Litmus .....	sharp	indefinite	indefinite	indefinite
Phenolphthalein	sharp	sharp	sharp	sharp

Engel (*Compt. rend.*, 1886, 102, 262), too, has shown that when a solution of phosphoric acid is tritrated, it appears to be monobasic if methyl-orange is used as the indicator, but bibasic with phenolphthalein, and tribasic with Poirier's soluble



When heated at 200—210°, the disubstituted butanetetracarboxylic acids readily lose 2 mols. of carbonic anhydride, yielding disubstituted adipic acids.

The study of these disubstituted adipic acids is especially interesting in view of the recent work of Bischoff, Auwers and Victor Meyer Zelinsky, Perkin, and others, on the isomerism of  $\alpha\alpha$ -disubstituted acids in the succinic, glutaric, and pimelic series.

The symmetrical disubstituted succinic acids (Leuchart, *Ber.*, **18**, 2348; Zelinsky, *Ber.*, **21**, 3170; Bischoff and Voit, *Ber.*, **20**, 2988; Hell and Rothberg, *Ber.*, **22**, 66; Bischoff and Voit, *Ber.*, **22**, 389; Bischoff and Hjelt, *Ber.*, **21**, 2089, 2097, 2102; Bischoff, *Ber.*, **20**, 2988; Hjelt, *Ber.*, **20**, 3078; Bischoff and Mintz, *Ber.*, **23**, 650; Buitchichin and Zelinsky, *Abstr.*, 1889, 377; 1890, 740) are found to exist in two well marked isomeric forms; for instance, two dimethylsuccinic acids are known, melting at 123—124° and 192°, and two diethylsuccinic acids, melting at 129° and 192°. The isomerism of the disubstituted glutaric acids is, apparently, not so pronounced as that of the disubstituted succinic acids; of the dialkyl-glutaric acids (Zelinsky, *Ber.*, **22**, 2823; Bischoff, *Ber.*, **23**, 1465; Bischoff and Mintz, *Ber.*, **23**, 649; Auwers and Köbner, *Ber.*, **24**, 1933; Guthzeit and Dressel, *Annalen*, **256**, 171), the dimethyl derivatives alone have been separated into two distinct modifications, melting at 102—104° and 128° respectively. A number of disubstituted pimelic acids (Perkin and Prentice, *Trans.*, 1891, **59**, 818) have been prepared, but in no case could a separation into two isomerides be satisfactorily accomplished; it was, however, frequently noticed that the melting-points of the acids were not so sharp as could be desired, and there is reason to believe that these acids also occur in two isomeric forms, which are so similar in properties that separation is a matter of great difficulty.

Considerable interest, therefore, attaches to the question of isomerism in the disubstituted adipic acids, as these are intermediate between the glutaric and pimelic acids. It has been found in the course of the present research that these disubstituted adipic acids invariably exist in two modifications, which usually differ from one another in a

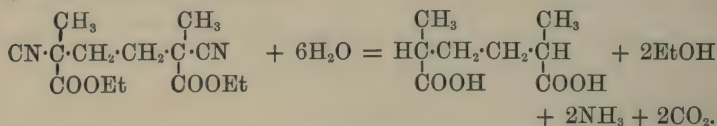
blue. He also showed that boric acid is neutral to methyl-orange, feebly acid to litmus or phenolphthaleïn, and acid to soluble blue. From these instances, it appears that litmus is liable to give lower results than phenolphthaleïn, and in the case of litmus the final colour change is usually very indefinite.

It also is evident that any knowledge of the basicity of an acid obtained by titration is only relative to the nature of the indicator employed, and, further, when a polybasic acid has been only partially neutralised, its acid function may be enfeebled altogether out of proportion to the amount of base which has been added to it. This raises the wider question of the basicity of polybasic acids, and of their affinity as a function of the affinities of the groups which they contain. (See "Note on the Affinities of Polybasic Acids," this vol., p. 1024.)



very marked manner in melting-point, solubility, and other physical properties.

For instance, the dimethyladipic acids melt at 70—72° and 142°, the diethyl at 51—53° and 136°, the dibenzyl at 152° and 211—213°. It is remarkable that the isomerism of these disubstituted acids is as pronounced in the adipic series as in the succinic, whilst in the intermediate glutaric series it is much less noticeable. Of these derivatives of adipic acid, the dimethyl alone have previously been obtained (Zelinsky, *Ber.*, **24**, 3997), through the hydrolysis of ethylic dicyanodimethyladipate with sulphuric acid, as represented by the equation—



It is a well-known fact that whilst oxalic acid, or malonic acid and its alkylic derivatives, do not form internal anhydrides, the formation of an anhydride occurs readily in the case of succinic acid, and it is exceedingly interesting that the introduction of alkylic groups much increases the tendency to form anhydrides (Bischoff and Mintz, *Ber.*, **23**, 620 and 656; Auwers and Jackson, *Ber.*, **23**, 1614); for instance, dimethylsuccinic acid yields an anhydride much more readily than succinic acid, and again anhydride formation takes place more readily in the alkylic derivatives of glutaric acid than in the case of the acid itself. Now adipic acid does not form an anhydride, but the introduction of methyl or other groups appears to increase the tendency to form an anhydride, and Manasse and Rupe (*Ber.*, **27**, 1818; 1894) have very recently succeeded in obtaining the anhydride of  $\beta$ -methyladipic acid; it is noteworthy that it is very unstable, and reverts to the acid on long exposure to the air. The disubstituted adipic acids, described in the following pages, when heated with acetyl chloride in sealed tubes, in no case gave an anhydride; in view, however, of the work of Manasse and Rupe (*loc. cit.*), it is possible that sufficient precautions were not taken to prevent the access of moisture from the air during the working up of the product; further experiments are in progress to decide this point.

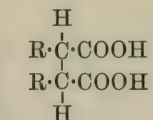
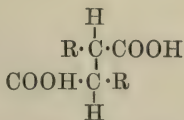
Whilst, however, no anhydride was formed on heating the disubstituted adipic acids in sealed tubes with acetyl chloride, it was found that, whether the higher-melting or lower-melting modification was employed, a partial conversion of the one into the other was effected, the product consisting of a mixture of the two. Similarly, when the symmetrical disubstituted succinic acids (Bischoff and

Mintz, *Ber.*, **23**, 656) are heated in sealed tubes at  $200^{\circ}$ , in each case a mixture of the two modifications of the acid is formed. A similar conversion can be effected in the case of the dimethylglutaric acids (Zelinsky and Besredka, *Ber.*, **24**, 465; Auwers and Köbner, *Ber.*, **24**, 1933).

It remains to refer to the theories which have been advanced to account for the two modifications of these symmetrical  $\alpha$ -disubstituted dicarboxylic acids. From the close analogy between the constitution of a symmetrical  $\alpha$ -dialkylsuccinic acid and that of a tartaric acid, each containing a pair of asymmetric carbon atoms, according to one view (Bischoff and Walden, *Ber.*, **22**, 1819), it has been held that any two isomeric symmetrical disubstituted succinic acids correspond to the two inactive tartaric acids, the one being inactive through intramolecular compensation of right- and left-handed groups, whilst the other consists of a mixture of equal quantities of the active right- and left-handed acids. If this is so, it should be possible to resolve one or other of the two substituted succinic acids into two active constituents. The chief objection which this theory has to meet is that hitherto in no case has this resolution into active forms been accomplished, although repeated attempts have been made in the case of the substituted succinic acids (Bischoff and Walden, *loc. cit.*).

As a result of this failure, a theory has been widely entertained of late, which draws an analogy between the saturated molecules of two isomeric symmetrical disubstituted succinic acids and the unsaturated molecules of fumaric and maleïc acids. According to this view, it is held that whilst, in general, a singly-bound atom or group can freely rotate, yet, under some circumstances, certain saturated molecules can be fixed in different phases. Thus, it is held that the disubstituted succinic acids

CHR·COOH  
|  
CHR·COOH may exist in two so-called stereochemical isomerides, of which the acid of lower-melting point usually gives an anhydride, and is therefore called the maleinoid or *cis* modification, whilst the acid of higher-melting point is incapable of forming an anhydride, and is named, on that account, the fumaroid or *trans*-modification. These two modifications may be represented thus.

Maleinoid or *cis*.Fumaroid or *trans*.

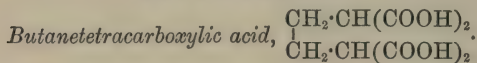
The isomerism in question, therefore, according to this view,

depends on the fixation of carbon atoms united by single bonds, and the acceptance of this view involves the removal of one of the fundamental ideas of van't Hoff's theory.

A third theory—known as the theory of dynamical isomerism—has been advanced by Bischoff (*Ber.*, **23**, 624), but as the compounds which led him to adopt it have since been found not to exist (Auwers and Jackson, *Ber.*, **23**, 1606), it has not met with general acceptance.

It only remains to add, before proceeding to describe these derivatives in detail, that no attempt has yet been made to resolve any of the dialkyladipic acids into active forms.

#### EXPERIMENTAL.



As it appeared interesting to endeavour to obtain this acid for comparison with the other tetracarboxylic acids described in this paper, pure ethylic butanetetracarboxylate (1 mol.) was hydrolysed by boiling it for six hours with a solution of barium hydroxide (8 mols.), and the crystalline precipitate of the barium salt collected upon a filter, washed with water, and decomposed with sulphuric acid. After the slight excess of sulphuric acid had been carefully precipitated with barium hydroxide, the clear aqueous solution of the carboxylic acid was evaporated first on the water-bath, and then over sulphuric acid; in two days, it had crystallised in part in a mass of prismatic needles. These were separated from the mother-liquor, spread on a porous tile, and after drying further over sulphuric acid, were found to melt gradually between 140° and 160°.

0.1618 gave 0.2520 CO<sub>2</sub>, and 0.0712 H<sub>2</sub>O; C = 42.47; H = 4.88.

C<sub>8</sub>H<sub>10</sub>O<sub>8</sub> requires C = 41.03; H = 4.27 per cent.

C<sub>7</sub>H<sub>10</sub>O<sub>8</sub>     ,,     C = 44.21; H = 5.26     ,,

As the analysis appeared to indicate that a mixture of the tetracarboxylic and tricarboxylic acids had been formed, an attempt was made to isolate the tetracarboxylic acid from the mother liquor referred to above. The aqueous solution was evaporated further until a second crop of crystals had been deposited; the small quantity of mother liquor still remaining was poured off from this, and evaporated over sulphuric acid until it had completely solidified to a porcelain-like mass; this product was found to melt gradually, and evolved carbonic anhydride between 115° and 148°; at the latter temperature adipic acid melts, being formed from the carboxylic acids by elimination of carbonic anhydride.



0.1567 gave 0.2471  $\text{CO}_2$ , and 0.0734  $\text{H}_2\text{O}$ ;  $\text{C} = 43.00$ ;  $\text{H} = 5.20$  per cent.

A *silver salt* was prepared by pouring a neutral solution of the ammonium salt into a large excess of silver nitrate solution and shaking well; the white precipitate was collected on a filter, well washed, and dried first on a porous tile, and then over sulphuric acid.

0.3022 gave 0.1921 silver;  $\text{Ag} = 63.06$ .

0.1074 „ 0.0953  $\text{CO}_2$  and 0.0211  $\text{H}_2\text{O}$ ;  $\text{C} = 15.15$ ;  $\text{H} = 1.36$ .

$\text{C}_8\text{H}_6\text{O}_8\text{Ag}_4$  requires  $\text{Ag} = 65.23$ ;  $\text{C} = 14.50$ ;  $\text{H} = 0.91$ .

$\text{C}_7\text{H}_7\text{O}_6\text{Ag}_3$  „  $\text{Ag} = 63.40$ ;  $\text{C} = 16.44$ ;  $\text{H} = 1.36$ .

It appears, therefore, that the butanetetracarboxylic acid, obtained by the hydrolysis of its ethylic salt with excess of barium hydroxide, is somewhat unstable, and tends to part with one molecule of carbonic anhydride, with formation of butanetricarboxylic acid. This instability of butanetetracarboxylic acid is in accordance with the character of its homologues. Conrad and Bischoff (*Annalen*, **214**, 71) have shown that ethanetetracarboxylic acid on hydrolysis with potassium hydroxide gives ethanetricarboxylic acid; Buchner (*Ber.*, **25**, 1157), however, found that the stability of the acid depends much on the concentration of the alkali, and if dilute sodium hydroxide be used, ethanetetracarboxylic acid may be isolated. Propanetetracarboxylic acid has been obtained by Kleber (*Annalen*, **246**, 107), who found that on slightly warming the aqueous solution of the acid, it is decomposed with evolution of carbonic anhydride. The hydrolysis of ethylic butanetetracarboxylate with alcoholic potash has been carried out by Perkin (*Trans.*, 1887, **51**, 19), and there was evidence of a partial conversion of the tetracarboxylic acid into the tricarboxylic acid; Perkin and Prentice (*Trans.*, 1891, **59**, 824), when hydrolysing ethylic pentanetetracarboxylate with alcoholic potash, obtained a similar result.

This mixture of butanetetracarboxylic acid and butanetricarboxylic acid is extremely soluble in water, giving a solution of intensely acid character. It is also very readily soluble in ether, and in methylic or ethylic alcohol, but insoluble in benzene, toluene, or light petroleum.

A neutral solution of the ammonium salts gives but a slight precipitate in the cold with barium chloride: on boiling, however, a copious white crystalline precipitate of the monobarium salts is thrown down. Calcium chloride gives no precipitate in the cold, but the calcium salts are precipitated on boiling, and dissolve again partially on cooling. Ferric chloride and copper acetate give no precipitate.





The quantities used in the preparation of this substance were—

Ethylic butanetetracarboxylate .....	35.0 grams
Sodium dissolved in 60 c.c. alcohol....	4.6 „
Methylic iodide .....,.....	28.4 „

The ethylic butanetetracarboxylate was dissolved in the sodium ethoxide, and the methylic iodide added slowly, since much heat is developed; it was then heated on the water-bath, using a reflux condenser, for about two hours, until it no longer gave an alkaline reaction. Water was then added, the product evaporated, extracted with ether, and the ethereal solution dried with calcium chloride. On distilling off the ether, and allowing the residual oil to stand some days, ethylic dimethylbutanetetracarboxylate crystallised out in beautiful prisms. It was collected on a filter, and washed with a little ether. For analysis, a portion was dried at 100°, and allowed to solidify.

0.1553 gave 0.3290 CO<sub>2</sub> and 0.1184 H<sub>2</sub>O. C = 57.75; H = 8.04

C<sub>18</sub>H<sub>30</sub>O<sub>8</sub> requires C = 57.75; H = 8.02 per cent.

The mother liquors from this substance, on standing, deposited a less pure product, which was used in the subsequent preparation of the dimethyladipic acids.

Ethylic dimethylbutanetetracarboxylate crystallises in beautiful, thick, four-sided prisms, melts at 54°, and is readily soluble in ether, methylic and ethylic alcohols, benzene, and toluene. It dissolves readily in warm light petroleum, and crystallises out again on cooling.



Ethylic dimethylbutanetetracarboxylate is not readily hydrolysed by barium hydroxide; in order to prepare the acid, the pure ethereal salt (1 mol.) was digested for three hours with an excess of a solution of pure potassium hydroxide (6 mols.) in methylic alcohol, in a flask connected with a reflux condenser. The product was evaporated nearly to dryness, mixed with water, the solution again evaporated to a small bulk to remove the last traces of alcohol, acidified with hydrochloric acid, and extracted four times with pure ether. On distilling off the ether, the dimethylbutanetetracarboxylic acid was left as a yellowish crystalline mass; this was purified by dissolving it in a little water, and allowing the solution to evaporate slowly over sulphuric acid in a vacuum, when the pure acid gradually crystallised

out as a mass of minute white needles. These were collected, dried on a porous tile, and over sulphuric acid in a vacuum, and analysed with the following result.

0.1014 gave 0.1698  $\text{CO}_2$  and 0.0528  $\text{H}_2\text{O}$ ;  $\text{C} = 45.67$ ;  $\text{H} = 5.78$ .

$\text{C}_{10}\text{H}_{14}\text{O}_8$  requires  $\text{C} = 45.80$ ;  $\text{H} = 5.35$  per cent.

Dimethylbutanetetracarboxylic acid is deposited as a felted mass of minute needles on slowly evaporating its concentrated aqueous solution. It decomposes at  $200^\circ$  with evolution of carbonic anhydride, is readily soluble in ether and in methylic or ethylic alcohol, but insoluble in benzene, toluene, and light petroleum.

The *basicity* of the acid was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.1763 gram of substance required 0.1480 gram of KOH for neutralisation, phenolphthaleïn being used as the indicator: the final colour change was sharp. A quadribasic acid of the formula  $\text{C}_6\text{H}_{10}(\text{COOH})_4$  requires 0.1507 gram of KOH to form a salt of the formula  $\text{C}_6\text{H}_{10}(\text{COOK})_4$ . On adding one or two drops of litmus solution to the solution of the quadribasic salt, which was neutral as indicated by phenolphthaleïn, there was a very distinct blue coloration, which only gradually became red on running in hydrochloric acid. It appears, therefore, that dimethylbutanetetracarboxylic acid forms quadribasic salts, which are neutral to phenolphthaleïn, but alkaline to litmus.

*Silver Salt*,  $\text{C}_{10}\text{H}_{10}\text{O}_8\text{Ag}_4$ .—The acid was dissolved in dilute ammonia, and the solution placed over sulphuric acid in a vacuum. As soon as it was only slightly alkaline to litmus it was poured into a large excess of silver nitrate solution in a flask, and the mixture well shaken. The white precipitate was collected on a filter, well washed with water, and dried on a porous tile and over sulphuric acid in a vacuum.

Analysis proved the salt to be quadribasic.

0.1048 gave 0.0650 Ag;  $\text{Ag} = 62.02$ .

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{Ag}_4$  requires  $\text{Ag} = 62.60$  per cent.

If a solution of calcium chloride is added to a cold neutral solution of the ammonium salt no precipitate is formed, but on heating a crystalline precipitate of the *calcium salt* is thrown down.



When heated with sulphuric acid, ethylic dimethylbutanetetracarboxylate is readily hydrolysed, but at the same time it loses 2 mols. of carbonic anhydride and yields a mixture of dimethyladipic acids. The ethereal salt was therefore heated on a sand-bath in a reflux

apparatus with equal parts of sulphuric acid and water for about three hours. On allowing the mixture to cool, a considerable quantity of dimethyladipic acid crystallised out.

*Isolation of the modification of higher-melting point.*—The acid which had crystallised on cooling was washed with a little water, dissolved in a solution of sodium carbonate, boiled with animal charcoal, and filtered; the filtrate was then acidified with hydrochloric acid, and the dimethyladipic acid which separated, collected on a filter, washed with a little water, and recrystallised from water. This acid melted at 130—135°, and as it was found to be only sparingly soluble in boiling benzene, it was digested two or three times with small quantities of boiling benzene, and the benzene solution in each case poured off as completely as possible. The acid which still remained undissolved was recrystallised from water, and dried at 100°. It was then found to melt sharply at 142°.

Analysis showed it to consist of pure dimethyladipic acid.

0.1504 gave 0.1129 H<sub>2</sub>O and 0.3053 CO<sub>2</sub>; C = 55.36; H = 8.34.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.18; H = 8.04 per cent.

This acid has already been prepared by Zelinsky (*Ber.*, **24**, 3997), by the hydrolysis of ethylic dicyanodimethyladipate.

*Isolation of the modification of lower-melting point.*—The hot benzene solutions obtained in the isolation of the modification of dimethyladipic acid of higher-melting point, on cooling, deposited crystals which consisted chiefly of this modification. When these were removed, and the benzene evaporated on the water-bath, a yellowish, viscid oil was obtained, which crystallised completely on cooling, and melted at 80—90°. It was digested with a small quantity of cold benzene, the solution filtered from undissolved matter, and the benzene evaporated; the crystalline residue, on being again submitted twice to the same treatment, left a nearly colourless crystalline mass which melted at 70—72°, and was found by analysis to consist of pure dimethyladipic acid.

0.1383 gave 0.2805 CO<sub>2</sub> and 0.1028 H<sub>2</sub>O; C = 55.31; H = 8.26.

C<sub>8</sub>H<sub>14</sub>O<sub>4</sub> requires C = 55.18; H = 8.04 per cent.

Zelinsky (*loc. cit.*), who separated the two isomeric dimethyladipic acids by recrystallisation from water, gives the melting-point of this dimethyladipic acid as 74—76°.\*

\* Since the printing of the thesis, Zitzing (*Ber.*, **27**, 1578; 1894) has described the preparation of ethylic dimethylbutanetetracarboxylate by the action of ethylenic dibromide on the monosodium derivative of ethylic methylmalonate, and he has prepared from it dimethylbutanetetracarboxylic acid and two dimethyladipic acids.

B. *Ethylic Diethylbutanetetracarboxylate*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CEt}(\text{COOEt})_2 \\ | \\ \text{CH}_2 \cdot \text{CEt}(\text{COOEt})_2 \end{array}$

The following quantities were employed in the preparation of this substance:

Ethylic butanetetracarboxylate.....	70.0 grams
Sodium dissolved in 120 c.c. alcohol .	9.2 „
Ethylic iodide .....	70.0 „

The ethylic butanetetracarboxylate was dissolved in the sodium ethoxide, and the ethylic iodide added cautiously with constant cooling, as much heat is evolved; the mixture was then heated for two hours on the water-bath, using a reflux condenser, and to ensure the completion of the action a little more ethylic iodide was added, and the digestion continued for two hours longer.

The product, mixed with water and evaporated to remove alcohol, gave a beautifully crystalline cake on cooling; this was separated from the mother liquor, dissolved in ether, and the ethereal solution, after being well washed with water, was dried with calcium chloride. On slowly evaporating the ethereal solution, the ethylic diethylbutanetetracarboxylate separated in fine silky needles.

For analysis, the ethereal salt was recrystallised from ether, heated in a steam-oven to fusion, and allowed to solidify.

0.1307 gave 0.2865  $\text{CO}_2$  and 0.1030  $\text{H}_2\text{O}$ ; C = 59.78; H = 8.76.

$\text{C}_{20}\text{H}_{34}\text{O}_8$  requires C = 59.70; H = 8.45 per cent.

Ethylic diethylbutanetetracarboxylate crystallises from ether in fine silky needles, which melt at about 93—94°. It is readily soluble in hot methylic or ethylic alcohol, and crystallises out, on cooling, in fine needles. It is also readily soluble in cold benzene and toluene, and crystallises well from hot light petroleum.

*Diethylbutanetetracarboxylic acid*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CEt}(\text{COOH})_2 \\ | \\ \text{CH}_2 \cdot \text{CEt}(\text{COOH})_2 \end{array}$

Diethylbutanetetracarboxylic acid was obtained by the hydrolysis of its ethereal salt with barium hydroxide. As this takes place with some difficulty, the ethylic salt was heated with twice the theoretical amount of barium hydroxide, for two days on the sand-bath, using a reflux condenser; during the action, a strong menthol-like odour was observed. When the hydrolysis was complete, the heavy crystalline precipitate of barium diethylbutanetetracarboxylate was collected, and, after being washed with a little water, was ground up, suspended in water, and boiled for two hours with a slight excess of sulphuric acid so as to set free the diethylbutanetetracarboxylic acid. The



excess of sulphuric acid was exactly precipitated with barium hydroxide, and the aqueous solution evaporated to a small bulk on the water-bath; as the concentration proceeded, the acid crystallised in beautiful slender needles; these were collected on a filter, washed with a little water, and spread on a porous plate. On determining their melting-point, the acid frothed up in the capillary tube, and decomposed at 207—209°. After recrystallisation from water, the decomposing-point was unchanged. For analysis, the crystals were dried at 100°.

0.1442 gave 0.2619  $\text{CO}_2$  and 0.0850  $\text{H}_2\text{O}$ ;  $\text{C} = 49.53$ ;  $\text{H} = 6.54$ .

$\text{C}_{12}\text{H}_{18}\text{O}_8$  requires  $\text{C} = 49.66$ ;  $\text{H} = 6.20$ .

It is remarkable that diethylbutanetetracarboxylic acid is only sparingly soluble in water, whereas the corresponding dimethylbutanetetracarboxylic acid is so very readily soluble. It crystallises from its hot aqueous solution in needles, which decompose at 207—209°, with evolution of carbonic anhydride; it is soluble in ether, benzene, toluene, and light petroleum, and readily in methylic or ethylic alcohol.

The *basicity* of the acid was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.2139 gram of acid required 0.0850 gram of KOH for neutralisation, using litmus; litmus proved, however, a very unsatisfactory indicator, as, after dissolving the acid in excess of alkali, on titrating back with hydrochloric acid, the blue tint changed only gradually to red. An acid of the formula  $\text{C}_8\text{H}_{14}(\text{COOH})_4$  would require 0.0826 gram of KOH to form the bibasic salt,  $\text{C}_8\text{H}_{14}(\text{COOH})_2(\text{COOK})_2$ .

A determination was also made in which phenolphthalein was used as the indicator.

0.2114 gram of acid required 0.1656 gram of KOH for neutralisation. An acid of the formula  $\text{C}_8\text{H}_{14}(\text{COOH})_4$  would require 0.1632 gram of KOH to form the quadribasic salt,  $\text{C}_8\text{H}_{14}(\text{COOK})_4$ . The solution of the acid in potassium hydroxide, after it had been neutralised with hydrochloric acid as shown by phenolphthalein, was coloured distinctly blue on the addition of one or two drops of litmus solution.

It appears, therefore, that diethylbutanetetracarboxylic acid, like dimethylbutanetetracarboxylic acid, forms quadribasic salts, which are neutral to phenolphthalein, but alkaline to litmus, the bibasic salt being neutral to litmus.

*Silver salt*,  $\text{C}_{12}\text{H}_{14}\text{O}_8\text{Ag}_4$ .—This was prepared exactly in the manner described on p. 1005, but it was found impossible to analyse it by ignition in a combustion furnace or in a crucible, as it decomposes with a rapidity which is almost explosive. The silver was therefore estimated as silver chloride. Analysis proved the salt to be quadribasic.

0.1180 gave 0.0935 AgCl; Ag = 59.57.

$C_{12}H_{16}O_8Ag_2$  requires Ag = 42.86 per cent.

$C_{12}H_{14}O_8Ag_4$  „ Ag = 60.17 per cent.

The silver salt decomposes slowly on exposure to light.

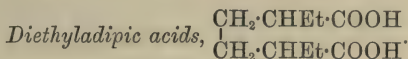
*Calcium salt*,  $C_{12}H_{14}O_8Ca_2 + 5H_2O$  (?).—If calcium chloride is added to a cold neutral solution of ammonium diethylbutanetetra-carboxylate there is no precipitate, but, on boiling, a white micro-crystalline precipitate of the calcium salt is at once thrown down; this was collected on a filter, and dried on a porous plate. For analysis, the salt was dried by exposure to the air for four days.

As the quantity available for analysis was very small, it was impossible to determine the water of crystallisation accurately. An estimation of the calcium proved the salt to be tetrabasic, and indicated that it probably contains 5 mols. of water of crystallisation. Heated at  $150^\circ$ , the calcium salt lost more than 15 per cent. in weight, through the elimination of a portion of its water of crystallisation. It did not decompose when heated to  $160^\circ$ .

0.1083 gave 0.0630  $CaSO_4$ ; Ca = 17.11.

$C_{12}H_{16}O_8Ca$  requires Ca = 12.19.

$C_{12}H_{14}O_8Ca_2 + 5 H_2O$  requires Ca = 17.54;  $H_2O$  = 19.53 per cent.



In order to prepare these acids, the pure diethylbutanetetra-carboxylic acid was heated in an oil-bath at  $210^\circ$  until the evolution of carbonic anhydride had completely ceased. On cooling, the product solidified to a brownish crystalline cake.

*Isolation of the modification of higher-melting point.*—This brownish product was digested with boiling water, filtered while hot, and allowed to cool, when a considerable quantity of diethyladipic acid crystallised out in fine white needles; this, when separated from the mother-liquor, and dried on a porous plate, was found to melt at  $122$ — $129^\circ$ ; after three more crystallisations the crystals melted sharply at  $136^\circ$ , and the melting-point was not altered by further crystallisation. An analysis proved it to be pure diethyladipic acid.

0.1503 gave 0.3257  $CO_2$  and 0.1178  $H_2O$ ; C = 59.10; H = 8.70.

$C_{10}H_{18}O_4$  requires C = 59.40; H = 8.92 per cent.

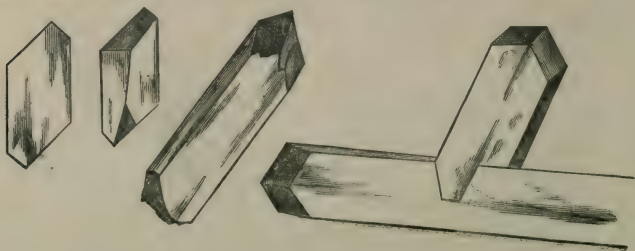
*Isolation of the modification of lower-melting point.*—This proved to be a matter of greater difficulty. The aqueous mother-liquors, obtained in the isolation of the acid melting at  $136^\circ$ , were extracted three times with ether, and the ethereal solution evaporated; the yellowish oily residue after a time deposited a few stellate groups of

crystals, and at the end of two days the oil had completely solidified. A small portion, after drying on a porous plate, was found to melt at  $55\text{--}105^\circ$ . The solubilities of this crude product, and of the pure acid melting at  $136^\circ$ , in various solvents, were then carefully compared, and it was found that the former was readily soluble in cold benzene, whilst the acid melting at  $136^\circ$  was only sparingly soluble in boiling benzene. Accordingly, the crude acid melting at  $55\text{--}105^\circ$  was ground up and digested with cold benzene, and the solution filtered from a small quantity of undissolved acid, which, after drying, melted at  $130\text{--}132^\circ$ . The benzene solution evaporated on the water-bath, yielded a yellowish viscid mass, which crystallised when exposed over sulphuric acid in a vacuum; it melted at  $45\text{--}60^\circ$  after it had been left on a porous plate for a time. The product was again digested with cold benzene, and the solution worked up in the same manner; on repeating the process, using little more than its own volume of benzene, a crystalline mass was finally obtained which melted at  $45\text{--}46^\circ$ . As the acid had still a yellowish tint, an attempt was made to purify it by means of the calcium salt. The acid was therefore digested with a large volume of lime water, and after carbonic anhydride had been passed through the solution, the filtrate was concentrated until the greater portion of the calcium salt had crystallised, and only about 2 c.c. of yellowish mother-liquor were left. The crystalline salt was collected on a filter, and washed with a little cold water. To obtain the pure diethyladipic acid, the calcium salt was dissolved in water, decomposed with hydrochloric acid, and extracted with ether; the ethereal solution when dried over anhydrous calcium chloride, evaporated, and exposed in a vacuum over sulphuric acid, left a colourless oil which gradually solidified to a mass of characteristic stellate groups of acicular crystals melting at  $51\text{--}53^\circ$ . For analysis, the acid was heated to fusion in a steam-oven, and allowed to solidify.

0.1218 gave 0.2631  $\text{CO}_2$  and 0.0987  $\text{H}_2\text{O}$ ;  $\text{C} = 58.91$ ;  $\text{H} = 9.00$ .

$\text{C}_{10}\text{H}_{18}\text{O}_4$  requires  $\text{C} = 59.40$ ;  $\text{H} = 8.92$  per cent.

*Properties of the Diethyladipic acid melting at  $136^\circ$ .*—This acid crystallises in six-sided prisms of the following form.





The *silver salt*,  $C_{10}H_{16}O_4Ag_2$ , was formed by dissolving the acid in slight excess of ammonia, and, after removing this excess by evaporation over sulphuric acid, adding excess of silver nitrate solution, when the silver salt was thrown down as a voluminous white precipitate. This was collected on a filter, washed with water, and dried first on a porous plate, and then over sulphuric acid in a vacuum.

0.1644 gave 0.0848 Ag; Ag = 51.58.

$C_{10}H_{16}O_4Ag_2$  requires Ag = 51.92 per cent.

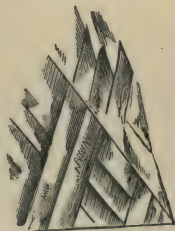
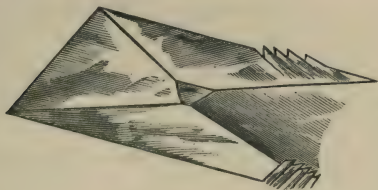
The *calcium salt*,  $C_{10}H_{16}O_4Ca + 2H_2O$ , was also prepared by dissolving the acid in a large quantity of water, adding excess of calcium hydroxide, and boiling the solution; the excess of calcium hydroxide was removed by passing carbonic anhydride through the solution, which was again boiled, filtered, and evaporated on the water-bath; as the concentration proceeded, calcium diethyladipate crystallised out in beautiful white prisms. It was dried by exposure to the air for five days.

0.3155, on drying at  $150^\circ$ , lost 0.0398  $H_2O$ ; the anhydrous salt so obtained gave 0.1613  $CaSO_4$ ;  $H_2O = 12.61$ ; Ca = 15.03.

$C_{10}H_{16}O_4Ca + 2H_2O$  requires  $H_2O = 13.04$ ; Ca = 14.49 per cent.

Unfortunately too little of the salt was left to allow of a second analysis. The calcium salt is very sparingly soluble in water.

*Properties of the Diethyladipic acid melting about  $51-53^\circ$ .*—This acid crystallises after fusion in large sub-octahedral masses, composed of interlacing needles, of the following form.



The formation of the *calcium salt* has already been described. It is more soluble in water than the calcium salt of the isomeric acid, which melts at  $136^\circ$ .

The *silver salt*,  $C_{10}H_{16}O_4Ag_2$ , was formed by the double decomposition of the aqueous solution of the calcium salt with silver nitrate solution; the precipitate, after being well washed, was dried on a porous plate and in a vacuum over sulphuric acid.

0.2450 gave 0.2535  $CO_2$ , 0.0852  $H_2O$ , and 0.1276 Ag; C = 28.22; H = 3.86; Ag = 52.07.

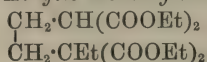
$C_{10}H_{16}O_4Ag_2$  requires C = 28.84; H = 3.84; Ag = 51.92 per cent.



The solubility of the two modifications of adipic acid in various solvents may be conveniently recorded in tabular form.

Solvent.	Solubilities of the two diethyladipic acids.	
	Diethyladipic acid melting at 136°.	Diethyladipic acid melting at 51—53°.
Ether .....	Readily soluble in the cold.	Readily soluble in the cold.
Methylic alcohol...	Readily soluble in the cold.	Readily soluble in the cold.
Ethylic alcohol ....	Readily soluble in the cold.	Readily soluble in the cold.
Benzene .....	Very sparingly soluble; soluble in a large quantity of boiling benzene, and precipitated in minute needles on cooling.	Readily soluble in the cold.
Toluene.....	Sparingly soluble in the cold; readily soluble in hot toluene, and partially precipitated in crystals on cooling.	Readily soluble in the cold.
Light petroleum ...	Insoluble even on boiling.	Soluble with difficulty on boiling, and partially precipitated in very minute needles on cooling.
Water.....	Soluble in much cold water; crystallises from a little hot water on cooling.	Readily soluble in the cold.

*Attempt to prepare Ethylic Monethylbutanetetracarboxylate,*



In this communication, the preparation of several disubstituted derivatives of ethylic butanetetracarboxylate is described, and it appeared of interest to ascertain whether monosubstituted derivatives would be obtained if the monosodium derivative of this substance were employed.

The following quantities were taken—

Ethylic butanetetracarboxylate .....	35.0 grams.
Sodium dissolved in 30 c.c. alcohol ...	2.3 „
Ethylic iodide .....	15.6 „

The ethylic butanetetracarboxylate was dissolved in the sodium ethoxide, and the ethylic iodide added gradually; at first there was little evolution of heat, but, on shaking, the mixture became quite hot. It was heated on the water-bath for  $2\frac{1}{2}$  hours, using a reflux condenser, the product evaporated on the water-bath, water added, and the evaporation repeated. The residue was then extracted

three times with ether, the ethereal solution washed with water, dehydrated with calcium chloride, and the ether evaporated first on the water-bath, and finally by exposure in a vacuum. In this way, about 35 grams of a yellowish oil were obtained, which deposited about 10 grams of crystals; these were separated from the mother-liquor by filtration with the pump, and freed from oil by spreading upon a porous plate. The product melted at  $92-93^{\circ}$ , and after repeated crystallisation from methylic alcohol the melting point remained constant at  $93-94^{\circ}$ . On analysis, it proved to be ethylic diethylbutanetetracarboxylate, corresponding with it in melting-point, crystalline form, and every other respect.

0.1641 gave 0.3601  $\text{CO}_2$  and 0.1246  $\text{H}_2\text{O}$ ;  $\text{C} = 59.84$ ;  $\text{H} = 8.43$ .

$\text{C}_{18}\text{H}_{30}\text{O}_8$  requires  $\text{C} = 57.75$ ;  $\text{H} = 8.02$ .

$\text{C}_{20}\text{H}_{34}\text{O}_8$  „  $\text{C} = 59.70$ ;  $\text{H} = 8.45$  per cent.

It is evident, therefore, that the main product of the action was the diethyl-, and not the monethyl-derivative of ethylic butanetetracarboxylate.

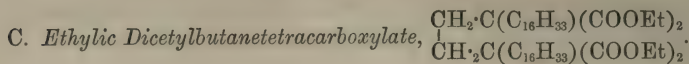
To determine the nature of the 25 grams of yellowish oil from which the ethylic diethylbutanetetracarboxylate had crystallised, and which should consist, if the above conclusion is correct, of unchanged ethylic butanetetracarboxylate, together with a certain amount of its diethyl derivative in solution, the oil was hydrolysed with barium hydroxide.

The 25 grams of oil were boiled with a concentrated solution of 75 grams of barium hydroxide for two days; a slight excess of sulphuric acid was then added to liberate the organic acids, and the filtered solution extracted 20 times with ether. The last 15 extracts were worked up together, and, after evaporating the ether, gave a nearly-colourless oil, which crystallised on standing. This product was heated at  $210^{\circ}$  in an oil-bath until the evolution of carbonic anhydride had ceased, and the residual dark-coloured oil, which solidified on cooling, after being spread on a porous plate, was dissolved in a little hot water, and allowed to evaporate slowly over sulphuric acid; the colourless crystalline deposit which formed was collected, and dried over sulphuric acid. It melted at  $148^{\circ}$ , and consisted of pure adipic acid, as is shown by the following analysis.

0.1441 gave 0.2613  $\text{CO}_2$  and 0.0901  $\text{H}_2\text{O}$ ;  $\text{C} = 49.45$ ;  $\text{H} = 6.94$ .

$\text{C}_6\text{H}_{10}\text{O}_4$  requires  $\text{C} = 49.31$ ;  $\text{H} = 6.86$  per cent.

It appears, therefore, that, under the conditions employed, ethylic monethylbutanetetracarboxylate is not formed, the interaction, on the contrary, giving rise to ethylic diethylbutanetetracarboxylate, one half of the ethylic butanetetracarboxylate remaining unchanged.



The following quantities were used in the preparation of this substance,

Ethyl butanetetracarboxylate .....	35.0	grams.
Sodium dissolved in 120 c.c. alcohol ..	4.6	„
Cetyl iodide.....	76.0	„

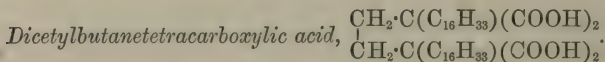
The ethyl butanetetracarboxylate was dissolved in the cold solution of sodium ethoxide, the cetyl iodide added cautiously, and the mixture well shaken; no appreciable rise of temperature occurred; the mixture was then heated for six hours on the water-bath, using a reflux condenser. After cooling and standing over night, a considerable quantity of a crystalline powder had separated. The contents of the flask were mixed with water, gently heated on the water-bath to remove alcohol, and then extracted four times with ether. The ethereal extract was washed with water, dried with calcium chloride, and the ether distilled off, when about 60 grams of a dark oily liquid remained; this, after some days, deposited a considerable quantity of a yellowish, soap-like mass, which was separated from the oil by aid of the pump, spread upon a porous plate, and crystallised once or twice from light petroleum. The ethyl dicetylbutanetetracarboxylate was thus obtained pure in glistening white crystals.

For analysis, the crystals were heated to 100°.

0.1092 gave 0.2908 CO<sub>2</sub> and 0.1117 H<sub>2</sub>O; C = 72.62; H = 11.36.

C<sub>48</sub>H<sub>90</sub>O<sub>8</sub> requires C = 72.54; H = 11.33 per cent.

Ethyl dicetylbutanetetracarboxylate crystallises from light petroleum in small, four-sided plates, which melt at 69.5°. It is readily soluble in ether, benzene, and toluene, and in hot light petroleum, glacial acetic acid, and methylic or ethylic alcohol; on cooling, it crystallises again from all these solvents.



To prepare this acid, pure ethyl dicetylbutanetetracarboxylate (1 mol.) was digested for about four hours with an excess of a solution of pure potassium hydroxide (6 mols.) in methylic alcohol, in a flask connected with a reflux condenser. After standing over night, a quantity of potassium dicetylbutanetetracarboxylate had crystallised out; this was collected, dissolved in hot water, and acidified with hydrochloric acid, when dicetylbutanetetracarboxylic acid separated as an oil, which, on cooling, solidified to a hard, white, non-

crystalline cake. To free the acid from traces of potassium chloride the cake was kneaded with a little water, extracted with ether, and the ethereal solution washed with water. After removal of the ether by evaporation, and drying by exposure in a vacuum over sulphuric acid, pure dicetylbutanetetra-carboxylic acid was obtained as a beautiful, white, non-crystalline mass. It was found necessary to follow the above method, starting with pure material and utilising only the purest products, in order to prepare *pure* dicetylbutanetetra-carboxylic acid, as no solvent was found by means of which the crude acid could be purified by crystallisation.

On analysis—

0.0990 gave 0.2552  $\text{CO}_2$  and 0.1007  $\text{H}_2\text{O}$ ;  $\text{C} = 70.30$ ;  $\text{H} = 11.17$ .

$\text{C}_{40}\text{H}_{74}\text{O}_8$  requires  $\text{C} = 70.38$ ;  $\text{H} = 10.85$  per cent.

A further quantity of dicetylbutanetetra-carboxylic acid, sufficiently pure for subsequent operations, was obtained from the crude dark-coloured oily product, referred to as being obtained in the course of the preparation of pure ethylic dicetylbutanetetra-carboxylate. After hydrolysis of the oil with alcoholic potash, water was added, and the alcohol removed by evaporation on the water-bath. On cooling, almost the whole of the potassium dicetylbutanetetra-carboxylate separated as a yellow saponaceous mass, which was freed from cetylic iodide, cetylic alcohol, cetene, and other impurities, by repeatedly digesting it with ether until it became almost colourless. The free acid obtained from this potassium salt was an almost colourless mass.

Dicetylbutanetetra-carboxylic acid is a white soap-like body, which has not been obtained in a crystalline form. It does not possess a sharp melting-point, melting gradually between  $80^\circ$  and  $90^\circ$ , and when heated to  $150^\circ$ , decomposes with rapid evolution of carbonic anhydride. It is readily soluble in benzene, toluene, light petroleum, ether, and glacial acetic acid, insoluble in water, and concentrated hydrochloric and hydrobromic acids. It is readily soluble in cold ethylic alcohol, but in methylic alcohol its solubility varies extraordinarily within a very small range of temperature. Thus, whereas at  $23^\circ$ , 100 grams of methylic alcohol will dissolve 4.2 grams of the acid, at  $19^\circ$  only 1.9 grams of the acid are retained in solution.

The *basicity* of the acid was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.2141 gram of substance required 0.0701 gram of KOH for neutralisation, phenolphthalein being used as the indicator. A quadribasic acid of the formula  $\text{C}_{40}\text{H}_{74}\text{O}_8$  would take 0.0703 gram of KOH to form the quadribasic salt  $\text{C}_{36}\text{H}_{70}(\text{COOK})_4$ . On adding 1 or 2 drops of litmus solution to the solution of the quadribasic



salt, which was neutral as indicated by phenolphthaleïn, a very distinct blue coloration appeared, which only gradually became red as hydrochloric acid was run in.

It appears, therefore, that dicetylbutanetetracarboxylic acid, like diethyl- and dimethyl-butane-tetracarboxylic acids, forms quadribasic salts, which are neutral to phenolphthaleïn, but alkaline to litmus.

*Salts of Dicetylbutanetetracarboxylic acid.*—In connection with the results obtained when determining the basicity of the acid, it appeared of interest to examine some of its salts.

*Calcium salt,  $C_{40}H_{72}O_8Ca$ .*—The acid was dissolved in dilute ammonia, and the excess of ammonia removed by evaporation, until the solution was but very slightly alkaline to litmus; excess of calcium chloride was then added, and the mixture well shaken. The white precipitate, collected on a filter, washed with water, and dried on a porous plate, was freed from a trace of colouring matter by crystallising it from boiling ethylic alcohol, from which it separated in needles.

For analysis, the salt was dried in the air for six days.

(1.) 0.3176 gave 0.0462  $CaSO_4$ ;  $Ca = 4.31$ .

(2.) 0.2887 „ 0.0424 „ „ 4.32.

(3.) When heated at  $100^\circ$ , the calcium salt slowly loses weight, becoming slightly viscid, and undergoes slow decomposition, so that it may possibly contain water or alcohol of crystallisation.

$C_{40}H_{72}O_8Ca$  requires  $Ca = 4.83$  per cent.

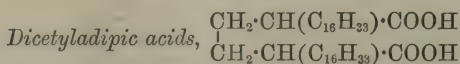
It thus appears that the calcium salt which is formed under the above conditions is bibasic. It is insoluble in water, somewhat readily soluble in ether, but only sparingly in ethylic alcohol.

*Silver salt,  $C_{40}H_{72}O_8Ag_2$ .*—The solution of the ammonium salt, which was neutral as indicated by litmus, was poured into excess of silver nitrate solution, and the mixture well shaken. The insoluble silver salt which was thrown down was collected on a filter, well washed, and dried on a porous plate and over sulphuric acid.

0.1068 gave 0.0260 silver;  $Ag = 24.34$ .

$C_{40}H_{72}O_8Ag_2$  requires  $Ag = 24.11$  per cent.

The silver salt formed under the above conditions appears, therefore, to be bibasic. It is unstable, and quickly blackens on exposure to light.



Pure dicetylbutanetetracarboxylic acid was heated in an oil-bath at  $205^\circ$  until carbonic anhydride was no longer evolved; on cooling, a

rather brown, non-crystalline cake was formed. With the exception of ether and methylic and ethylic alcohols, it is sparingly soluble in the usual solvents; in methylic or ethylic alcohol it is readily soluble on warming, separating again in an amorphous form on cooling; consequently the purification and isolation of the two isomeric dicetyladiptic acids is a matter of some difficulty. It was found advantageous to purify the mixture of the isomeric acids by digestion with ethylic alcohol and animal charcoal; after filtration, an almost colourless product separated on cooling, which melted gradually between  $30^{\circ}$  and  $40^{\circ}$ .

*Isolation of the modification of higher melting-point.*—The product melting at  $30$ — $40^{\circ}$  was dissolved in hot ethylic alcohol, and the mass which separated on cooling, after drying on a porous plate and by exposure over sulphuric acid in a vacuum, was found to melt at  $38$ — $42^{\circ}$ ; on repeating this treatment, a substance was obtained which melted at  $41$ — $43^{\circ}$ , and subsequent recrystallisation did not raise the melting-point.

I. 0.1208 gave 0.3420  $\text{CO}_2$  and 0.1355  $\text{H}_2\text{O}$ ;  $\text{C} = 77.21$ ;  $\text{H} = 12.46$ .  
 II. 0.1227 „ 0.3490 „ 0.1380  $\text{H}_2\text{O}$ ;  $\text{C} = 77.54$ ;  $\text{H} = 12.49$ .  
 $\text{C}_{42}\text{H}_{62}\text{O}_4$  requires  $\text{C} = 77.53$ ;  $\text{H} = 12.62$  per cent.

From the results of the analysis, it appeared that the substance melting at  $41$ — $43^{\circ}$  was not a dicetyladiptic acid, but its ethylic salt, formed by the repeated solution of the acid in hot ethylic alcohol, and this was rendered the more probable by its behaviour on hydrolysis. To obtain the acid itself, the ethereal salt was hydrolysed with alcoholic potash; the alcohol was evaporated on the water-bath, hydrochloric acid added, and the product extracted with ether; after washing the ethereal solution with water, the ether was evaporated on the water-bath, and the white mass obtained was dried by exposure over sulphuric acid in a vacuum; the melting-point, namely,  $40$ — $43^{\circ}$ , was scarcely altered, but analysis proved it to be dicetyladiptic acid.

0.1138 gave 0.3203  $\text{CO}_2$  and 0.1267  $\text{H}_2\text{O}$ ;  $\text{C} = 76.76$ ;  $\text{H} = 12.37$ .  
 $\text{C}_{38}\text{H}_{74}\text{O}_4$  requires  $\text{C} = 76.77$ ;  $\text{H} = 12.46$  per cent.

*Isolation of the modification of lower melting-point.*—In the isolation of the modification of higher melting-point, the substance melting at  $30$ — $40^{\circ}$ , obtained by heating dicetylbutanetetra-carboxylic acid at  $210^{\circ}$ , was dissolved in hot ethylic alcohol; the mass which separated on cooling melted at  $38$ — $42^{\circ}$ , but the mother liquor, on standing a day or two, deposited a second crop, which was found to melt at  $33$ — $38^{\circ}$ . The mother liquor from this was concentrated, and on standing deposited a third crop, melting at  $29$ — $34^{\circ}$ ; this was

dissolved in a small quantity of alcohol, and the solution, after a time, deposited a pure white amorphous substance, which, when dried, melted at 32—34°.

On analysis—

0.1491 gave 0.4188 CO<sub>2</sub> and 0.1675 H<sub>2</sub>O; C = 76.65; H = 12.48.

C<sub>38</sub>H<sub>74</sub>O<sub>4</sub> requires C = 76.77; H = 12.46 per cent.

It is noteworthy that the lower-melting dicetyl adipic acid, unlike the modification of higher melting-point, does not appear to form an ethereal salt when repeatedly dissolved in ethylic alcohol, though it is more readily soluble in the latter.

D. *Ethylic Dibenzylbutanetetracarboxylate*,  $\begin{matrix} \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7)(\text{COOEt})_2 \\ | \\ \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7)(\text{COOEt})_2 \end{matrix}$ .

The quantities used in the preparation of this substance were,

Ethylic butanetetracarboxylate .....	35.0 grams.
Sodium dissolved in 60 c.c. alcohol ...	4.6 „
Benzyl chloride .....	30.0 „

The ethylic butanetetracarboxylate was dissolved in the cold solution of the sodium ethoxide; the benzyl chloride was then cautiously added, and the mixture after shaking became perceptibly warm. The whole was then heated on the water-bath for about two hours, using a reflux condenser to complete the action. The contents of the flask were mixed with water, and distilled with steam until the alcohol and excess of benzyl chloride were removed; on cooling, the crystals which gradually separated were collected, washed with a little water, and dried on a porous plate. They were then dissolved in ether, the ethereal solution washed with water, dehydrated with anhydrous potassium carbonate, and the ether evaporated until the dibenzyl-derivative began to separate. On standing, a plentiful crop of small white crystals of pure ethylic dibenzylbutanetetracarboxylate was obtained; on analysis,

0.1934 gave 0.4830 CO<sub>2</sub> and 0.1282 H<sub>2</sub>O; C = 68.09; H = 7.34.

C<sub>30</sub>H<sub>38</sub>O<sub>8</sub> requires C = 68.44; H = 7.22 per cent.

Ethylic dibenzylbutanetetracarboxylate crystallises in small four-sided tabular crystals. It is readily soluble in boiling methylic or ethylic alcohol, from which it crystallises on cooling. It is somewhat more sparingly soluble in ether and in light petroleum, from both of which it crystallises on cooling. It dissolves in warm benzene, but does not separate out on cooling. When crystallised from ethylic alcohol, it melts at 126—127°.

*Dibenzylbutanetetra-carboxylic acid*,  $\begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7)(\text{COOH})_2 \\ | \\ \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7)(\text{COOH})_2 \end{array}$ .

This acid is formed by the hydrolysis of ethylic dibenzylbutane-tetracarboxylate with alcoholic potash. About 36 grams of the pure ethereal salt (1 mol.) were heated for two hours on the water-bath with a solution of 24 grams of potassium hydroxide (6 mols.) in methylic alcohol, in a flask connected with a reflux condenser. After cooling, and standing over night, a considerable quantity of potassium dibenzylbutanetetra-carboxylate separated in the crystalline form; the alcoholic solution was filtered off, and worked up independently. The crystalline potassium salt was dissolved in water, and concentrated hydrochloric acid added, when the dibenzylbutanetetra-carboxylic acid separated in a semi-solid state, and after standing for a short time solidified to a hard white crystalline cake. This was separated from the mother-liquor, washed with water, dried on a porous plate, and purified by repeated crystallisation from 75 per cent. acetic acid, until the melting-point was constant. It was found necessary to crystallise the acid six or seven times.

For analysis, the acid was dried on a porous plate, heated at 100° in an air-bath, and finally placed over potassium hydroxide in a vacuum, to ensure the removal of traces of acetic acid, which were retained somewhat persistently.

- I. 0.1491 gave 0.3477  $\text{CO}_2$  and 0.0763  $\text{H}_2\text{O}$ ; C = 63.59; H = 5.68.  
 II. 0.1483 „ 0.3450 „ 0.0754  $\text{H}_2\text{O}$ ; C = 63.44; H = 5.64.  
 III. 0.1591 „ 0.3727 „ 0.0773  $\text{H}_2\text{O}$ ; C = 63.88; H = 5.39.  
 $\text{C}_{22}\text{H}_{22}\text{O}_8$  requires C = 63.77; H = 5.31 per cent.

A further quantity of less pure acid was obtained from the alcoholic mother-liquors previously referred to above; these were mixed with water, and after evaporating on a water-bath until free from alcohol, concentrated hydrochloric acid was added, when the dibenzylbutanetetra-carboxylic acid separated as a heavy oil; this, when extracted with ether, &c., in the usual way, left the acid as a thick brownish oil, which did not solidify, even after standing for days over sulphuric acid in a vacuum. This crude acid was, however, sufficiently pure for conversion into dibenzyladipic acids as described in the next section.

Dibenzylbutanetetra-carboxylic acid crystallises from dilute acetic acid in beautiful white plates, which, on exposure over potassium hydroxide in a vacuum, slowly lose weight, apparently from loss of acetic acid of crystallisation; after heating for a few minutes at 100°, the acid melts at 166—167°, with evolution of carbonic anhydride.



Heated at 100—105°, it is very slowly converted into dibenzyladipic acids. It is readily soluble in cold ether, and in methylic or ethylic alcohol, also in hot benzene or toluene, and more sparingly in light petroleum, from which it crystallises on cooling. It is soluble in hot acetic acid, and crystallises out partially on cooling, but much more completely on the addition of water, as it is very sparingly soluble in water.

The *basicity of the acid* was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.1800 gram of the acid required 0.0486 gram of KOH for neutralisation, as indicated by litmus. An acid of the formula  $C_{18}H_{18}(COOH)_4$  would take 0.0974 gram of KOH to form the quadribasic salt, or 0.0487 gram of KOH to form the bibasic salt.

A determination was also made in which phenolphthaleïn was used as the indicator. 0.2389 gram of the acid required 0.0678 gram of KOH for neutralisation, as indicated by phenolphthaleïn; on adding a drop or two of litmus to the colourless solution, it was coloured distinctly blue, and two or three drops of N/10 hydrochloric acid were necessary to render the solution neutral to litmus. An acid of the formula  $C_{18}H_{18}(COOH)_4$  would require 0.0646 gram of KOH to form the bibasic salt  $C_{18}H_{18}(COOH)_2(COOK)_2$ .

Whilst, therefore, phenolphthaleïn and litmus did not give absolutely identical results, it appears that dibenzylbutanetetracarboxylic acid tends to form neutral bibasic salts.

*Salts of Dibenzylbutanetetracarboxylic acid.*—In view of the result obtained on titrating the acid, it was thought advisable to examine some of its salts, in order to determine whether these were bibasic or quadribasic.

*Calcium Salt*,  $C_{22}H_{20}O_8Ca + 2H_2O$ .—About 2 grams of the acid were boiled with excess of calcium hydroxide, and the excess of lime precipitated by passing a stream of carbonic anhydride through the solution; the product was boiled and filtered, and the filtrate evaporated to a small bulk. The calcium salt which crystallised out was collected in a filter, and dried on a porous plate.

For analysis, the salt was dried by exposure to the air for six days. 0.3689, on heating at 110° till constant, lost 0.0286  $H_2O$ ;  $H_2O = 7.75$ . 0.2838 salt gave 0.0788  $CaSO_4$ ;  $Ca = 8.17$ .

$C_{22}H_{20}O_8Ca + 2H_2O$  requires  $Ca = 8.23$ ;  $H_2O = 7.37$  per cent.

The calcium salt, which is formed in the above manner, appears therefore to be bibasic, crystallising probably with  $2H_2O$ . It loses its water of crystallisation very slowly over sulphuric acid in a vacuum; when heated at 150°, it gradually decomposes.

*Silver Salt*,  $C_{22}H_{20}O_8Ag_2$ .—Excess of silver nitrate solution was

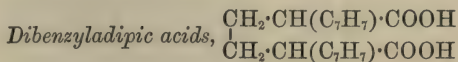
added to a neutral solution of the calcium salt. The white precipitate was collected on a filter, well washed with water, and dried on a porous plate and finally over sulphuric acid.

Analysis proved the salt to be bibasic.

0.4038 gave, on ignition, 0.1389 silver;  $\text{Ag} = 34.40$ .

$\text{C}_{22}\text{H}_{20}\text{O}_8\text{Ag}_2$  requires  $\text{Ag} = 34.55$  per cent.

The same silver salt is obtained on precipitating a neutral solution of the ammonium salt with silver nitrate solution; it is somewhat soluble in water, and decomposes readily when exposed to the light.



The impure oily dibenzylbutanetetracarboxylic acid (p. 1019) was heated in an oil-bath at  $200^\circ$  till all evolution of carbonic anhydride had ceased; on cooling, the impure dibenzyladipic acid solidified to a crystalline cake. The purification of this crude product, and the separation of the isomeric acids, is a somewhat difficult matter, and is best effected by means of their barium salts. About  $1\frac{1}{2}$  times the theoretical quantity of barium hydroxide was dissolved in a considerable quantity of water, and boiled with the crude dibenzyladipic acids for  $2\frac{1}{2}$  hours. As the barium salts thus formed remain dissolved if the solution is sufficiently dilute, the hot liquid was filtered, and a current of carbonic anhydride passed through the solution to remove the excess of barium hydroxide. The solution was filtered, the precipitated barium carbonate washed repeatedly with water, and the colourless filtrates concentrated on the water-bath until about one-half of the barium salts present had crystallised out. The glistening white plates thus obtained were rapidly filtered from the mother-liquor (the barium salts are less soluble in hot water than in cold), dissolved in water, and concentrated hydrochloric acid added, when the dibenzyladipic acids were thrown down as a white, microcrystalline precipitate; this was collected on a filter, washed with a little water, and dried on a porous plate; the melting-point was found to be  $190\text{--}210^\circ$ . After recrystallising three times from glacial acetic acid, a crop was obtained which melted at  $207\text{--}211^\circ$ ; the mother-liquors were concentrated to a small bulk, and the acid which crystallised out again removed; the filtrate was then heated to boiling, and diluted with hot water until a cloudiness began to appear; on cooling, crystals were formed, which melted at  $153\text{--}165^\circ$ . The solubilities of the two crops melting at  $207\text{--}211^\circ$  and  $153\text{--}165^\circ$  respectively were then compared in several solvents, and it was found that the one melting at  $207\text{--}211^\circ$  was practically insoluble in boiling toluene, whilst that melting at  $153\text{--}165^\circ$  dis-

solved readily, and in large measure crystallised out again on cooling.

To isolate the modification of dibenzyladipic acid of higher melting-point, the crop melting at  $207\text{--}211^\circ$  was digested with boiling toluene, and the undissolved acid collected on a filter, washed, and dried; on repeating this process several times, the final product melted constantly at  $211\text{--}213^\circ$ . Analysis proved it to consist of pure dibenzyladipic acid.

0.1440 gave  $0.3893\text{ CO}_2$  and  $0.0892\text{ H}_2\text{O}$ ;  $\text{C} = 73.73$ ;  $\text{H} = 6.88$ .

$\text{C}_{20}\text{H}_{22}\text{O}_4$  requires  $\text{C} = 73.62$ ;  $\text{H} = 6.75$  per cent.

To isolate the modification of lower melting-point, the product melting at  $153\text{--}165^\circ$  was recrystallised twice from toluene and then once from dilute acetic acid, when the acid was obtained in beautiful, colourless prisms melting sharply at  $152^\circ$ . It gave the following numbers on analysis.

0.1494 gave  $0.4028\text{ CO}_2$  and  $0.0913\text{ H}_2\text{O}$ ;  $\text{C} = 73.53$ ;  $\text{H} = 6.79$ .

$\text{C}_{20}\text{H}_{22}\text{O}_4$  requires  $\text{C} = 73.62$ ;  $\text{H} = 6.75$  per cent.

The mother liquor from the barium salts of the two acids gave a much larger quantity of the modification of lower melting-point.

*Properties of the dibenzyladipic acid melting at  $211\text{--}213^\circ$ .*—This acid is deposited from its glacial acetic acid solution in clusters diamond-shaped crystals of the following form.

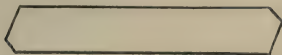
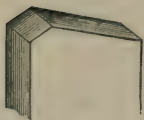


The *silver salt*,  $\text{C}_{20}\text{H}_{20}\text{O}_4\text{Ag}_2$ , which is very stable, was prepared from the ammonium salt in the same way as the other silver salts (p. 1011). It gave the following numbers on analysis.

0.2056 gave  $0.0821$  silver;  $\text{Ag} = 39.93$ .

$\text{C}_{20}\text{H}_{20}\text{O}_4\text{Ag}_2$  requires  $\text{Ag} = 40.00$  per cent.

*Properties of the dibenzyladipic acid melting at  $152^\circ$ .*—This acid crystallises from dilute acetic acid in six-sided prisms of the following form.



The *silver salt*,  $C_{20}H_{20}O_4Ag_2$ , was prepared in the same way as the other silver salts, and analysed with the following result.

0.2620 gave 0.1049 Ag on ignition. Ag = 40.03.

$C_{20}H_{20}O_4Ag_2$  requires Ag = 40.00.

It is somewhat soluble in hot water, and blackens rapidly on exposure to light.

The *solubility* of the two dibenzyladipic acids in various solvents may be conveniently recorded in tabular form.

Solvents.	Solubilities of the two dibenzyladipic acids.	
	Dibenzyladipic acid melting at $211-213^\circ$ .	Dibenzyladipic acid melting at $152^\circ$ .
Ether .....	Soluble in the cold.	Readily soluble in the cold.
Methylic alcohol ..	Soluble in the cold.	Readily soluble in the cold.
Ethylic alcohol ....	Soluble in the cold.	Readily soluble in the cold.
Benzene .....	Insoluble.	Soluble on heating; the acid is not precipitated on cooling.
Toluene .....	Only slightly soluble on boiling.	Readily soluble on warming; on cooling the acid crystallises out again.
Light petroleum ...	Insoluble.	Insoluble.
Water .....	Insoluble.	Insoluble.
Glacial acetic acid..	Very sparingly soluble in the cold; on boiling it dissolves readily, and on cooling crystallises out again.	Readily soluble in cold acetic acid; it is precipitated in a crystalline form on adding water.

It will be seen from the above table that the two dibenzyladipic acids differ markedly in their degree of solubility in benzene, toluene, and glacial acetic acid; the acid melting at  $152^\circ$  being much the more soluble of the two.

The author desires particularly to thank Professor W. H. Perkin, jun., for the fruitful suggestion which led to this research, and for the encouragement which was given whilst it was in progress.

*Organic Laboratory,  
Owens College, Manchester.*





NOTE ON THE AFFINITIES OF POLYBASIC  
ACIDS.

BY

BEVAN LEAN, D.Sc., B.A.

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[From the Transactions of the Chemical Society, 1894.]



## Note on the affinities of polybasic acids.

By BEVAN LEAN, D.Sc., B.A.

LIEBIG, in 1838, after a study of a number of organic acids, laid down as the criterion of polybasicity the capability of forming salts with different metallic oxides. The theory of polybasic acids was further developed by Laurent and Gerhardt, and later by Wurtz and Kekulé, and, as a result of their labours, the basicity of an acid has been regarded as determined by the number of stages in which the hydrogen can be displaced, or, in other words, by the number of salts it can form with a specified monad metal. More recently the researches of Thomsen and Ostwald have furnished other methods by which the basicity of acids can be determined, and in other ways have enlarged our knowledge of this class of compounds.

It is here desired to call attention to facts which show that the affinity of a polybasic acid is a complex function of the several affinities of all the groups contained within its molecule.

In the first place, it is to be observed that the thermal effects of the interaction of the first, second, &c., equivalents of a base with an acid, are not necessarily the same—on the contrary, they are, in general, different. The following instances may be quoted from Thomsen's work.

	Heat produced on neutralisation of acids.			
	Sulphuric.	Oxalic.	Succinic.	Phosphoric.
1st NaOH.....	14,750	13,850	12,400	14,850
2nd NaOH.....	16,650	14,450	11,750	12,250
3rd NaOH.....	—	—	—	6,950

Although these numbers sufficiently indicate the basicity of the acids, it is now recognised that the heats of neutralisation of the aqueous solutions of the acids do not represent exactly the quantities of heat liberated by the interaction of the acid with the base. Secondary actions often occur, such as the dissociation of the salts and formation of hydrates, so that the thermal effect is only the final resultant. To avoid these sources of error, Berthollet (*Ann. Chim. Phys.* [5], 4, 122 and 130) showed, several years ago, that it is sufficient to refer all the compounds to the solid state. Some determinations which Massol (*Compt. rend.*, 112, 1062) made in this direction in 1891, are particularly worthy of attention. He measured the



heats of neutralisation of the first and second molecules of a base with the molecules of bibasic acids of the oxalic acid series, the product being the solid salts. He obtained the following results.

	Oxalic.	Malonic.	Succinic.	Sulphuric.
1st KOH.....	34,280	27,870	25,260	47,800
2nd KOH.....	24,690	20,700	21,150	33,600

The particular point of importance in these observations is that in every case the second molecule of the base liberates *less* heat than the first, whilst in measurements of the heat of neutralisation in aqueous solution the reverse was frequently observed by Thomsen. Massol pointed out that whilst the heat developed on neutralising formic acid by potassium hydroxide is 25,800 units when the solid salt is formed, oxalic acid, which may be regarded as a carboxylic derivative of formic acid, has more than twice as great a heat of neutralisation, as though the two carboxyl groups effect a mutual strengthening of one another. It is seen from the above table that, when one of these carboxyls is neutralised, the acid salt acts like formic acid, and has almost the same heat of neutralisation. The results, then, at which he arrived, Massol attributed to a reciprocal action between the acid groups—an action which is less in degree in malonic and succinic acids, in which the carboxyl groups are farther apart from one another.

Berthelot, in a note to Massol's paper, pointed out that the greater development of heat by the first molecule of base is a necessary consequence of the fact (*Ann. Chim. Phys.* [5], 4, 130) that a bibasic acid interacts with its own normal salt forming an acid salt with development of heat.

Reverting now to the researches of Ostwald and his collaborators on the electrolytic conductivity of carboxylic acids, many facts are

Monobasic acids.*		Bibasic acids.†	
Formic acid .....	0·0214	Oxalic acid .....	10·
Acetic „ .....	0·00180	Malonic acid .....	0·171‡
Propionic acid .....	0·00134	Succinic „ .....	0·00665
Butyric „ .....	0·00149	Glutaric „ .....	0·00475
Valeric „ .....	0·00161	Adipic „ .....	0·00371
Hexylic „ .....	0·00145	Pimelic „ .....	0·00357

\* Ostwald, *Zeit. physikal. Chem.* (1889), 3, 174.

† Ostwald, *ibid.* (1889), 3, 271.

‡ Bethmann, *ibid.* (1890), 5, 402.

found which have significance in the present connection. The table (p. 1025) has been drawn up to show the relations between the "dissociation constants" of organic acids of the acetic and oxalic acid series.

Assuming that the "dissociation constants" of acids are a measure of their affinities, it is seen at once that as the homologous series are ascended the affinity of the acid decreases, and that by introducing a second carboxyl group into a monobasic acid the affinity of the acid is in every case more than doubled, indicating a mutual strengthening influence of the two carboxyls on one another, and it is also seen that this influence decreases in extent as the distance between the two groups is increased. Such an increase in the affinity of one carboxyl group by the introduction of another is parallel to the increase which is effected in phenol by the introduction of chlorine atoms or nitro-groups.

The influence of the introduction of alkyl groups into bibasic acids of the oxalic acid series has been studied by Bethmann (*Zeit. physikal Chem.*, 1890, **5**, 403), Walden (*ibid.*, 1892, **8**, 433), and Walker (*Trans.*, 1892, **61**, 696). The following tables of "dissociation constants" have been compiled from their papers.

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Malonic acid, 0·171.

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Methyl- .....	0·086	Dimethyl- .....	0·076
Ethyl- .....	0·127	Diethyl- .....	0·74
Propyl- .....	0·113	Dipropyl- .....	—
Benzyl- .....	0·151	Dibenzyl- .....	4·1

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Succinic acid, 0·00665.

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			Anti.	Para.
Methyl- .....	0·0086	Dimethyl- .....	0·0122	0·0204
Ethyl- .....	0·0085	Diethyl- .....	0·0245	0·0343
Propyl- .....	0·0089	Methylbenzyl- .....	—	0·0219
Benzyl- .....	0·0091	Ethylbenzyl- .....	—	0·0261

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Glutaric acid, 0·00475.

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			Anti.	Para.
Methyl- .....	0·0052	Dimethyl- .....	0·0053	0·0055
Ethyl- .....	—	Diethyl- .....	0·0055	0·0055
		Methylpropyl- .....	—	0·0059

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Pimelic acid, 0·00357.

	Dimethyl-* .....	0·00339
	Diethyl-.....	0·00345
	Dipropyl- .....	0·0032
	Dibenzyl- .....	0·0048

Although there are some irregularities which require explanation, the figures in the above tables bring out clearly the fact that an increase in the conductivity of a bibasic acid is effected by the introduction of alkyl groups, and the heavier the group the greater is its influence. The benzyl group on account of its mass, but probably more by reason of its acid character, appears to have an especial influence on the conductivity. Further, as the distance between the two carboxyls is increased, the effect of the introduction of alkyl groups is diminished.

In view of the relations which have already been brought out, it is of great interest to compare the constants of tetracarboxylic acids with those of the corresponding dicarboxylic acids. The only cases which appear to have been investigated hitherto are the dimethyl- and diethyl-derivatives of pentanetetracarboxylic acid; in each case, as Walker has found, the affinity of the acid is enormously increased by the close proximity of the two carboxylic groups at either end of the molecular chain.

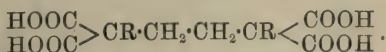
	Pimelic acid.	Pentanetetracarboxylic acid.	Ratio.
Dimethyl- .....	0·00339	0·37	1 : 109
Diethyl- .....	0·00345	2·1	1 : 608

The new dialkyl-derivatives of adipic acid and of butanetetracarboxylic acid, described in the preceding paper, are now in the hands of Dr. J. Walker.

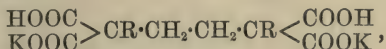
Other facts recorded in the preceding paper also have a bearing on the present subject. It was found that the quadribasic potassium salts of dimethyl-, diethyl-, and dicetyl-butanetetracarboxylic acids are alkaline to litmus, and the indefinite character of the final colour change showed that long before the theoretical quantity of alkali had been added, the acids had been almost completely neutralised; and, further, the neutral silver and calcium salts of dicetyl- and dibenzyl-butanetetracarboxylic acids were found to be bibasic. This fact, apparently so anomalous, is in measure understood on

\* The dialkylpimelic acids have not been separated into two modifications.

recalling that in the tetracarboxylic acids there are two carboxyl groups attached to one carbon-atom at either end of the molecular structure, thus



Such a juxtaposition of negative groups we have seen enormously increases the affinity of the acid, but so soon as a bibasic salt is formed, for instance



the strengthening influence of one carboxyl on another no longer exists, and instead we have the influence of the group COOK on the group COOH, with the result that the salt although dicarboxylic has little or no acid action. When R is the alkyl group methyl or ethyl, the bibasic salts have a slight acid action, and quadribasic salts were obtained; whereas when R is the heavier group, benzyl or cetyl, it was not found possible to prepare quadribasic salts.

The facts which have been adduced show clearly that the chemical activity of a polybasic acid is a complex function of the affinities of the several groups which it contains, and that the influence of one or more groups cannot be removed without affecting those of the rest. The chemical character in fact of an element or group of elements within a molecule depends not alone on itself, but also on the nature and position of those in the vicinity of which it is found.

*The Owens College,  
Manchester.*





$\beta$   $\beta$ -METHYLETHYLPROPIONIC ACID,  $\begin{matrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$

BY

W. H. BENTLEY, B.Sc.

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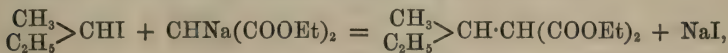
[From the Transactions of the Chemical Society, 1895.]



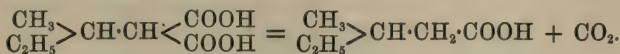
$\beta\beta$ -Methylethylpropionic acid,  $\begin{smallmatrix} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$ .

By W. H. BENTLEY, B.Sc.

DURING the course of experiments which are being carried on in the laboratories here, on the action of fused potash and soda on camphoric acid, various fatty acids have been obtained, and in order to determine their constitution, it was necessary to synthesise certain fatty acids hitherto unknown. At the suggestion of Dr. Perkin, I undertook the synthesis of  $\beta\beta$ -methylethylpropionic acid, and to study its properties. Methyl ethyl ketone was chosen as the starting point, and this was first reduced to methylethylcarbinol by the action of sodium on its moist ethereal solution, and the alcohol then converted into secondary butylic iodide,  $\text{CH}_3 \cdot \text{CHI} \cdot \text{C}_2\text{H}_5$ , by the action of iodine and phosphorus. This iodide, when treated with ethylic sodiomalonate, is readily converted into ethylic secondary butylmalonate,



which, on hydrolysis and subsequent distillation, yields  $\beta\beta$ -methyl-ethylpropionic acid, thus—



From the pure acid, which boils constantly at  $196^\circ$ , the following derivatives were prepared.

Ethylic salt, $\text{C}_5\text{H}_{11} \cdot \text{COOC}_2\text{H}_5$ .....	b. p. $157-158^\circ$ .
Amide, $\text{C}_5\text{H}_{11} \cdot \text{CO} \cdot \text{NH}_2$ .....	m. p. $125^\circ$ .
Anilide, $\text{C}_5\text{H}_{11} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ .....	„ $88^\circ$ .
Paratoluidide, $\text{C}_5\text{H}_{11} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ ....	„ $75^\circ$ .

*Methyl ethyl ketone*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_2\text{H}_5$ .—This was prepared by Böcking's



method (*Annalen*, 1880, **204**, 17), by the hydrolysis of ethylic methylacetate, by boiling it with one-fourth its weight of dilute sulphuric acid (20 per cent.) for six hours in a flask provided with a reflux condenser. The whole was then distilled in a current of steam, the distillate mixed with potassium carbonate, extracted several times with ether, and the ethereal solution washed successively with small quantities of water to remove alcohol; it was then dried with calcium chloride, and the fraction boiling at  $80-82^\circ$  collected.

*Secondary Butyl Alcohol; Methylethylcarbinol*,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}_2\text{H}_5$ .—The action of sodium amalgam on aqueous solution of the ketone gave such a small yield of methylethylcarbinol that this method was abandoned in favour of the following. The ketone was dissolved in five times its volume of ether, poured on to a strong solution of caustic soda contained in a bottle fitted with a reflux condenser, and small pieces of sodium were then dropped into the mixture; the white substance, which separated during the reduction, probably the sodium compound of the alcohol, was decomposed by the addition, from time to time, of small quantities of water, and the whole was kept cool by immersing the bottle in water. When about twice the theoretical quantity of sodium had been added, the ethereal solution was separated from the caustic soda, dried with potassium carbonate, and fractionated. The unreduced ketone was put back again into the bottle and treated with more sodium, whilst the fraction  $96-110^\circ$ , consisting chiefly of the alcohol, was carefully fractionated, the portion boiling at  $98-103^\circ$  being employed in the subsequent experiments; the boiling point of methylethylcarbinol, according to Lieben (*Annalen*, 1869, **150**, 114), is  $99^\circ$  (738.8 mm.).

*Secondary Butylic Bromide*,  $\text{CH}_3\cdot\text{CHBr}\cdot\text{C}_2\text{H}_5$ .—This substance, which does not seem to have been previously examined, was prepared by heating the alcohol with three times its volume of fuming hydrobromic acid for one hour in a reflux apparatus, a stream of hydrogen bromide being passed through the liquid during the operation. On adding water to the product, the bromide separated as a heavy oil. After drying over calcium chloride and fractionating, it boiled constantly at  $89-90^\circ$  and gave the following numbers on analysis.

Found .....	Br = 58.62
Theory for $\text{C}_4\text{H}_9\text{Br}$ .....	58.39.

*Secondary Butylic Iodide*,  $\text{CH}_3\cdot\text{CHI}\cdot\text{C}_2\text{H}_5$ , has been obtained from erythrol (De Luynes, *Bull. Soc. Chim.*, **2**, 3), from ethyldichloroether,  $\text{C}_2\text{H}_5\text{Cl}(\text{C}_2\text{H}_5)\text{O}\cdot\text{C}_2\text{H}_5$  (Lieben, *Annalen*, **150**, 96), and from normal butylene (Würtz, *Annalen*, 1869, **152**, 23), in each case by the action of hydriodic acid. As the result of several experiments, I found that the simplest way of preparing it was by treating secondary butyl

alcohol with iodine and phosphorus in the usual way. To the mixture of the alcohol (65 grams) with red phosphorus (10 grams), iodine (111 grams) was added in small quantities at a time. After standing for some time, the whole was heated in a reflux apparatus, distilled, and the distillate washed successively with a dilute solution of sodium hydrogen sulphite, and with water; it was then dried with calcium chloride and fractionated. The pure iodide is a colourless liquid boiling at  $118^\circ$ , the yield was almost quantitative.

*Ethyl Secondary Butylmalonate*,  $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CH}\cdot\text{CH}(\text{COOEt})_2$ .—In the first experiments made with the object of obtaining this compound, the bromide was employed; sodium (9 grams) was dissolved in alcohol, ethyl malonate (62 grams) added, and the mixture digested with secondary butyl bromide (53 grams), until the reaction was neutral. On adding water, extracting with ether, and distilling the washed and dried ethereal solution, the oily residue left when the ether had passed over distilled between  $195^\circ$  and  $198^\circ$ , and on examination was found to consist entirely of ethyl malonate. The bromide had evidently been decomposed into an unsaturated hydrocarbon and hydrogen bromide; and the latter, acting on the ethyl sodiomalonate, gave sodium bromide and ethyl malonate; this behaviour appears to be by no means uncommon, several other instances of a similar character having been observed here.

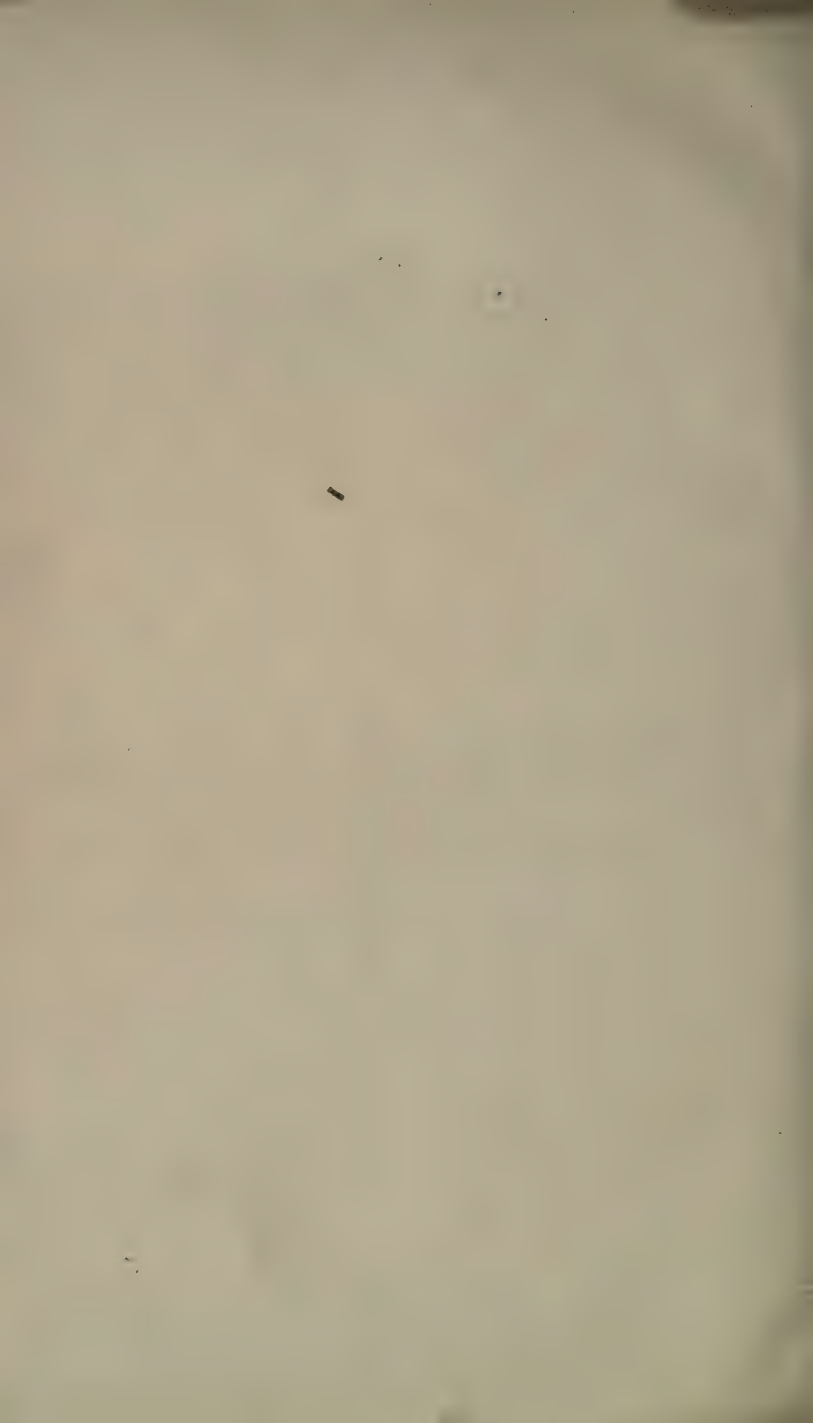
Subsequent experiments showed that secondary butyl iodide behaves in this respect quite differently from the bromide, as when digested in alcoholic solution with ethyl sodiomalonate, a very good yield of ethyl secondary butylmalonate is obtained.

Sodium (16 grams) was dissolved in ethyl alcohol (170 grams), ethyl malonate (109 grams) added, and the whole digested with secondary butyl iodide (125 grams) for two hours. The neutral product was cooled, diluted with 3 vols. of water, extracted with ether, and the ethereal solution distilled after being washed with water and dried with calcium chloride; the residue left, after the ether had passed over, was twice fractionated. The pure ethyl secondary butylmalonate thus obtained boiled at  $228$ – $231^\circ$ , and, on analysis, gave the following results.

Found . . . . . C =  $60\cdot54$ ; H =  $9\cdot21$  per cent.

Theory for  $\text{C}_{11}\text{H}_{20}\text{O}_4$  C =  $61\cdot11$ ; H =  $9\cdot26$  „

*Secondary Butylmalonic acid*,  $\begin{smallmatrix} \text{CH}_3 \\ | \\ \text{C}_2\text{H}_5 \end{smallmatrix} > \text{CH}\cdot\text{CH}(\text{COOH})_2$ .—In order to prepare this acid, the purified ethereal salt was boiled with an excess of alcoholic potash for two hours, the product diluted with water, and evaporated until all the alcohol had been removed. The solution was then acidified and extracted with ether, and the









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